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FOREWORD

Cooperation and exchange of scientific information under the US-USSR Agreement on Cooperation in the Field of Environmental Protection has helped both countries in their efforts to control environmental pollution. Among several working groups and projects established under this Agreement is Project 02.03-31, "Forms and Mechanisms by Which Pesticides and Chemicals are Transported in Soil, Water, and Biota." Members of this project and invited experts from government research organizations, academia, and private industry from the two countries have exchanged visits on several occasions. This document presents the proceedings of a project symposium held on October 21-27, 1981, in Yerevan, USSR.

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Director
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PREFACE

Under the USA-USSR Agreement on Cooperation in the Field of Environmental Protection, Soviet and American scientists, begining in 1974, are carrying on the work within the framework of the project 02.03-31 "Forms and Mechanisms by Which Pesticides and Chemicals Are Transported". Co-Chairmen of the project are George Baughman, US Side and Vladimir Borzilov, USSR Side (until 1982, David Duttweiler, US Side and Spartak Malakhov, USSR Side). The Institute of Experimental Meteorology is the head Soviet institution under the project.

The main purpose of the project is to develop prediction models of the behavior of pesticides and other chemicals in soil and water.

The first stage of cooperation, i.e. familiarization with research works under the project in both countries, was completed for the most part in 1976 when a 7-day symposium on the Environmental Transport and Transformation of Pesticides was held. Beginning in 1977, the studies are being carried out under the project on the agreed programs with the aim of developing and improving the mathematical models, establishing the dependences of their parameters on environmental characteristics, and testing the models under laboratory and field conditions. Part of the work has been performed independently in each country, and part - during the exchange visits of scientists to the United States and the Soviet Union. The results of the cooperative work were appraised in the Protocol of the eleventh meeting of the Soviet and American scientists engaged in the project (October 1981, USSR) as follows: "The work carried out under the project and planned for the future is very important from the practical point of view and beneficial for both sides because it provides results that cannot be obtained by one side alone".

Some scientific outcomes of the work were reviewed at the second symposium on the Prediction of Pesticide Behavior in the Environment, which was hosted by the Armenian Hydrometeorological Administration at Yerevan, October 21-27, 1981. Eleven American scientists (head of the delegation G. Bailey) and more than thirty Soviet scientists (head of the delegation V. Voloschuk) heard ten papers from the American side, sixteen papers from the Soviet side and one joint paper.

Based on the Synopsis of the symposium that recommended to develop physical-mathematical models of chemicals behavior and to test them, the program of future cooperation was worked out.

It includes continuation of joint research on:

- role of the components of natural waters in the kinetics of pollutant transformation;
- improvement of the technique for predicting the kinetics of microbial degradation;
- prediction of the kinetics of pesticide degradation in soil;
- improvement and field testing of the ARM, EXAMS and similar models for predicting the behavior of pollutants in soil and water.

V.M. Voloschuk, V.A. Borzilov

ABSTRACT

Under the USA-USSR Agreement on Cooperation in the Field of Environmental Protection, a joint project committee on forms and mechanisms by which pesticides and chemicals are transported sponsored a symposium on October 21-27, 1981, in Yerevan, USSR. Papers were presented by American and Soviet scientists on predicting pesticide behavior in soil and water. Twenty-six papers encompassed reviews of the state of the art in each country and results of research on particular aspects of the topics.

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PRESENT REQUIREMENTS IMPOSED UPON PESTICIDES IN THE SOVIET UNION

by

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It is now generally acknowledged that all chemical compounds circulate in the environment (air, soil,plants,hydrosphere, hydrobionts,animals and humans). The duration of circulation is different for various compounds, and some unstable substances do not undergo all stages of the circulation. However, persistent substances and particularly those containing mercury, arsenic,lead,selenium,cadmium and other elements are capable of accumulating in particular environmental objects,thus adversely affecting them(2,9,I0,I9,20) . Such elements as cadmium,mercury, lead and arsenic have accumulated in the World ocean in fairly dangerous concentrations due to their bioconcentration in hydrobionts(I0) .

The circulation of pesticides in the environment occurs in a similar way(I0,26) . Substances with high volatility and low chemical persistence undergo relatively rapid degradation and do not accumulate in environmental objects, while rather stable and lipophilic substances accumulate most intensively in various hydrobionts (2,42) .For example, the coefficient of bioconcentration for rainbow trout is I24 for DDT; 5,360 for pentachlorophenol; 947 for carbaryl; and I0,000 for 2,5-dichloro-4-nitrosalicyl anilide(37) . This high bioconcentration of organochlorine compounds in hydrobionts and other environmental objects results in their accumulation in foodstuffs and even in their entry into human milk (29) , which is rather dangerous to infants.

From the above it follows that major requirements on pesticides are determined by their behavior in environmental objects. Therefore the problem of pesticide transformation in various environmental objects should be considered in greater detail.

It is common knowledge that as a simplification, by the environment is meant the crust of the Earth with the biosphere and outer space surrounding the globe and affecting the life processes. The biosphere comprises all living organisms including animals,microorganisms and plants, as well as residues of these organisms, both dead and undergoing various stages of decomposition and transformation to simple organic and inorganic compounds. Included are also all combinations of living and nonliving matter (atmosphere,hydrosphere and soil).

Atmosphere. Pesticides may enter the atmosphere directly when applied by spraying or dusting,using ground-based facilities and particularly aircraft, and also as a result of evaporation from the soil or water surfaces. Clearly, the largest amounts of pesticides enter the atmosphere when being applied, since pesticide evaporation from soil occurs much slower due to their partial adsorption by soil colloids. Therefore,one and the same compound will evaporate from the surface of soil with different composition at different rates. Besides,the rate of pesticide evaporation from soil is greatly affected by the nature of a substance and its ability to be adsorbed by soil colloids, as well as by the temperature and velocity of air motion over the soil surface (48) .

Among the major processes determining the fate of pesticides in the atmosphere are their diffusion to the upper layers, deposition to soil,sedimentation to water bodies,photochemical degradation,hydrolysis and oxidation by oxygen and ozone. Of particular interest are chemical transformations of pesticides, in most cases resulting in less toxic products compared to parent compounds. Among these are primarily reactions of water vapor hydrolysis and oxidation by oxygen and ozone (28) .Sometimes photochemical transformations of pesticides result in the formation of rather stable substances capable of persisting in the environment for a long time. For example, polychlorodiphenyls (28) and isomers I-chloro-2-(4-chlorophenyl)-2(2,4-dichlorophenyl)-ethylenes and 3,6,9,IO-tetrachlorophenanthrene(34) were found in the photochemical transformation of DDT and DDE. Photolysis of insecticidal derivatives of carbamic acid proceeds more easily yielding corresponding phenols and their derivatives (47) , wheras photolysis of pentachlorophenol results in almost complete degradation of the molecule (28) . As to 2,3,7,8-tetrachlorodibenzodioxin (28) ,it is partially dechlorinated in a solution of methanol to form a corresponding trichloro derivative.

Pesticide photolysis is a major pathway of their transformation in the atmosphere, along with dispersion in the upper atmospheric layers. Thus, natural pyrethrins are not used extensively for plant protection because of their low photochemical stability.

The second place is occupied by reactions of hydrolysis and oxidation which appear to be of prime importance for degradation of organophosphorus compounds in the atmosphere (38) Sometimes even more complicated processes occur, as in the case of photolysis of trifluralin,where azo- and azoxy-compounds were found to be formed(50) . Other forms of photochemical transformations of various classes of pesticides were also observed(46) .

Clearly,those pesticides should be preferable for practical application (other factors being equal) which decompose most rapidly to form nontoxic products.

Hydrosphere. Pesticides and other chemical compounds may enter water bodies either directly or from the atmosphere and soil,or else in the form of products of human and animal vital activity. Pesticides may arrive from the atmosphere with rainfall or through direct deposition in the form of drops and solid particles, as a result of wind drift from aerial and even ground spray or dust application to plants, and when applied directly to water bodies to control mosquitos and other harmful insects. After entering water bodies,pesticides undergo chemical (hydrolysis,oxidation and photochemical decomposition) and biochemical (uptake by hydrobionts and metabolic decomposition) transformations.

Toxicity to hydrobionts and ability for bioconcentration in plankton, vertebrate and invertebrate hydrobionts (I,I2,42) are important criteria to be taken into account when choosing pesticides,especially persistent ones which eventually can cause lethal effects if accumulated in the organism of hydrobionts. Of all insecticides, organochlorine chemicals accumulate most rapidly,whereas accumulation of organophosphorus compounds in fish and water is insignificant (39) . This has been pointed out both in the early (2,I0,26,42) and recent studies, resulting in a considerably decreased use organochlorine insecticides, and in bans on the use of DDT and several other organochlorine compounds in the Soviet Union. Along with pesticide bioconcentration of great importance are pathways of metabolism in various hydrobionts and its rate (6) related directly to pesticide accumulation in the hydrobionts and the rate of their removal. These factors can be determined using the method suggested by R.L.Metcalf and coworkers (26) for an artificial ecosystem.

Microbial degradation of pesticides occurs in bottom sediments as well. As a rule,the most rapid is metabolism of those pesticides which form hydrophilous products of metabolic transformations.

Based on the presently available data, all pesticides may be subdivided into the following six groups,as to their persistence in the hydrosphere and other environmental objects:

I - pesticides with a period of complete degradation over I8 months;
2 - pesticides with a degradation period up to I8 months;

3 - pesticides with a degradation period not over up to I2 months;
4 - pesticides with a degradation period of no longer than 6 months;
5 - pesticides with a degradation period of 3 months;
6 - pesticides with a degradation period under 3 months;

By degradation is generally meant the breakdown of a chemical under the influence of various chemical and biochemical factors of the biosphere yielding nontoxic products.

It should be noted that the degradation period of one and the same pesticide depends to a large extent on meteorological conditions, type of ecosystem, population of water body, composition and properties of bottom sediments. Ambient temperature and solar intensity also play an important part: the higher they are, the more rapidly the degradation processes occur for most pesticides in aquatic and other ecosystems. All the above factors should be taken into account when choosing pesticides for a given climatic zone. Clearly, those chemicals should be preferable which have a degradation period under 3 months and are incapable of accumulating in water and hydrobionts (6).

As an illustration, Table I shows the data on the degradation rates of various pesticides in river water (32).Organochlorine insecticides are most persistent in water,whereas derivatives of carbamic acid and organophosphorus compounds are hydrolyzed rather rapidly. A similar situation is observed when studying pesticide persistence in fish (42). The data on pesticide persistence in fish are given in Table 2.

It should be noted that organochlorine pesticides have much higher toxicity to fish compared to organophosphorus compounds and derivatives of carbamic acid (26). The data on the toxicity of organochlorine insecticides to freshwater and marine fish are given in Table 3, and those of organophosphorus and carbamate insecticides in Tables 4 and 5,respectively. Toxicity of some herbicides to fish (8) is shown in Table 6

It is seen from the tables that biological activity of various groups of compounds is strongly dependent on their structure and therefore, on the pathways of their metabolic transformations in the organism of hydrobionts and the ecosystem as a whole.

Naturally,the values given in Tables I to 6 are not absolute, since they are strongly dependent on experimental conditions and can vary over a wide range. Their relative character,however, is retained and may serve as a guide for comparing chemicals.

Soil. A most important environmental object is soil which forms a peculiar biogeochemical envelope, an essential component of the biosphere,where a great number and variety of living organisms are concentrated, as well as the products of their metabolism and die-off.Soil with soil-dwelling organisms

Table I. Pesticide degradation rates in river water

Pesticide	% of the initial amount	
	After 2 weeks	After 4 weeks
Hexachlorocyclohexane (BHC)	I00	I00
Dieldrin	I00	I00
DDT	I00	I00
Endrin	I00	I00
Endosulfan	30	5
Heptachlor epoxide	I00	I00
Phosphamide /Dimethoate/	I00	85
Fenthion	50	I0
Thiofos /Parathion/	50	30
Carbofos /Malathion/	25	20
Aminocarb	60	I0
Propoxur	50	30
Carbaryl	5	0
Fenuron	60	20
Monuron	40	30

Table 2. Persistence of pesticides in fish

Pesticide	Persistence	Pesticide	Persistence
Diquate	< 3 weeks	Endothal	< 3 weeks
Simazine	<72 hours	2,4 D	< I week
Sodium arsenite	>I6 weeks	Dichlorbenil	< 2 weeks
Diazinon	< I week	Dursban	< I week
Azinphos-methyl	< I week	Carbofos /Malathion/	<24 hours
Thiofos/Parathion/	< I week	Lindane	<48 hours
Methoxychlor	I week	Heptachlor	I month
Dieldrin	I month	Toxaphene	> 6 months
DDD	> 6 months	DDT	> 6 months

Table 3. Toxicity of organochlorine insecticides to fish

Insecticide	LC_{50}, mg/l	
	Freshwater fish	Marine fish
Aldrin	0.0052-0.0082	0.0028
Heptachlor	0.008-0.0I9	0.0033-0.025
DDT	0.00I6-0.005	0.0004-0.002
Dieldrin	0.00I4-0.0028	0.0055-0.007I
Lindane	0.027-0.087	0.03
Methoxychlor	0.03-0.075	0.055
Mirex	5	2
Penthachlorophenol (PCP)	0.052-0.II	-
Perthane	0.005	-
Toxaphene	0.0II-0.0I8	0.0000I-0.0055
Chlordane	0.0078-0.04	0.0055
Endosulfan	0.0I2	0.0006
Endrin	0.0004-0.0086	0.0006-0.0026

is an universal biological adsorbent and neutralizer of organic compounds, and the result is decomposition of most waste material arising from man's economic activities and its use as a source of carbon and other elements essential for vital activity of organisms (3,I0,I3,I4,I8,26) . Large concentrations in soil of various chemical substances with high biological activity can adversely affect the vital activity of soil organisms and have a detrimental effect on self-purification capacity of the biosphere(3,I3,I8) .

Pesticides are transformed most intensively by various soil microorganisms(4,5,I0,II,I5-I7,23,24,26,27,3I,33,36,44, 45,5I) which in most cases use them as a source of carbon. Pesticide degradation in soil can proceed both by the oxidation and reduction mechanisms, depending on conditions. Under aerobic conditions pesticide degradation occurs in most cases as a result of oxidation,whereas reduction reactions, such as transformation of DDT to DDD are possible only under anaerobic conditions.

When choosing pesticides,one should take into account not only their degradation rate in soil and other environmental objects but also their toxicity to useful soil organisms,

Table 4. Toxicity of some organophosphorus insecticides to fish

Insecticide	LC_{50}, mg/l	
	Freshwater fish	Marine fish
Azinphos-methyl	0.0I4-0.052	0.0055
Demeton	0.08I	0.55
Diamidafos	I-306	I
Diazinon	0.002-0.09	0.25
DDVP	0.48	0.55
Dicrotophos	6.3	I
Dimethoate	6-8.5	I
Disulfoton	0.04	0.74
Carbofos /Malathion/	0.I03-0.I7	0.57
Metafos /Methyl parathion/	2.7-5.7	I
Monocrotophos	4.0-4.9	I
Naled (I,2-Dibromo-2,2-dichloroethyl-0,0-dimethylphosphate)	0.08-0.33	0.55
Parathion	0.47-2	0.065
Trichloronate	0.24	0.32
Phosphamidon	8.0	I
Fenotrothion	0.7	I
Chlorofos /Dipterex/	0.26-I.4	I.00
Chlorpyrifos	0.0033	0.07
Chlorpyrifos,methyl	0.0I4	0.I5
Ethion	0.23	0.069

such as earthworms(26). Other factors being equal,preference should be given to those chemicals that are rather innocuous for the useful soil flora and fauna.

Along with studies on the behavior of pesticides in the atmosphere, hydrosphere and soil, of great importance, are

Table 5. Toxicity of some carbamates to fish

Carbamate	LC_{50} , mg/l	
	Freshwater fish	Marine fish
Aminocarb	-	I
Carbaryl	4.34 - II.2	I.75
Methiocarb	0.II-0.64	0.55
Mexacarb	I5	I
Propoxur	8.2	I

those in animals and plants that is essential to prevent their entry into man's food chains. It is necessary primarily to study a possibility of pesticide entry into the milk of domestic animals that is an essential food product of man,along with other milk products (2I,22,25,30,40) . In some cases, cats, rats, dogs, rabbits and other animals (25), rather than cows,are used as models for studying metabolism. Note that sometimes pesticide metabolism in the organism of birds goes through a somewhat different pathway than that of warm-blooded animals. It should be pointed out that more or less considerable amounts of organochlorine pesticides and polychlorinated biphenyls (49) have been found in food products up to the present time. A positive property of many pesticides is their capability (or that of their transformation products) to form in the organism of animals water-soluble conjugates which can be easily excreted (4I) . Many pesticides form conjugates with plant substances as well. These conjugates,however, are less mobile and in many cases are retained in a plant for a long time. Naturally, the use of these chemicals in rather considerable amounts is less advisable. It is interesting that until very recently some amounts of pesticides have been found in the human organism (43) .

Based on the foregoing, the following general requirements on pesticides can be formulated:

- moderate persistence in a soil-climatic zone;
- low toxicity to hydrobionts and other useful organisms dwelling in water bodies and soil;
- rapid degradation in water and soil yielding products which are harmless to useful organisms;
- the absence of cumulation in the organism of man and animals;
- the absence of remote adverse effects on man,animals

Table 6. Toxicity of some herbicides to fish

Herbicide	LC_{50}, mg/l	
	Freshwater fish	Marine fish
Amitrole	50	-
Atrazine	I2-26	I.0
Bensulide	0.8I	0.32
Bromoxynile	0.05	-
Butylate	5.5	I.0
2,4-D, Butyl ester	0.39-2	5
Dalapon	87	50
Dinoseb	0.07 -0.3	-
Diquat	I0	I
Dichlone	0.I2-0.34	-
Diuron	3-60	6.3
Molinate	0.46-I.3	I
Monuron	76	I6.3
Picloram	2I	-
Propachlor	0.I6	-
Simazine	25-I00	-
2,4,5-T (2,4,5-Trichlorophenoxyacetic acid)	I2-50	-
Sodium trichloracetate (TCA)	I00	I
Trifluralin	0.0I-0.09	-

and various useful organisms, when pesticides are used systematically for a long time;

- a possibility to use alternately chemicals belonging to various classes of compounds to prevent the occurrence of resistant forms of harmful organisms and the accumulation of the chemicals in the environment;

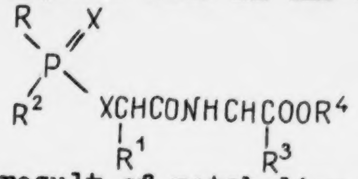
- maximum effectiveness against harmful organisms at lowest possible rates of application;

- sufficient safety of application and impossibility of acute poisoning;
- rather high economic efficiency of the use in agriculture and other fields;
- convinient and safe form of application.

When using pesticides in agriculture, of great importance is a correct determination of reentry period (time of waiting after pesticide application), as well as an accurate regulation of pesticide residues in food and forage crops to provide a safe use of agricultural products of plant and animal origin.

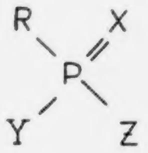
As an example of searching for new organophosphorus pesticides, we can mention two directions being developed in the Soviet Union.

First, synthesis of mixed ethers of phosphorus acids containing a peptide bond in the ether radical (35):



As a result of metabolism in environmental objects, these compounds form harmless amino acids and phosphoric acid which can be assimilated by various living organisms.

Second, synthesis of organic compounds of phosphorus with asymmetric carbon. Among these compounds are substances with different physiological activities, including insecticides, nematocides, fungicides and herbicides (7) :



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METABOLIC FATE OF PESTICIDES IN SOIL

by

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The soil serves as a massive reservoir for chemicals which reach it as unintentional and intentional contaminants. In order to predict the impact of those chemicals on the soil environment it is important to determine their degradative fate, establish metabolic pathways, and assess the ecotoxicological significance of the terminal degradation products remaining in the soil.

Physical modeling of pesticide degradation under controlled laboratory conditions is of immeasurable value in predicting behavior and fate under actual field conditions. Useful models for laboratory studies have been reported by several investigators, including: Bartha and Pramer (1965) (1); Lichtenstein and Fuhremann (1974) (2); Best and Weber (1974) (3); Bromilow and Leistra (1980) (4); Rhodes (1980) (5); Liang and Lichtenstein (1980) (6); Yockim et. al. (1980) (7); Guth (1980) (8) and 1981 (9); and Koeppe and Lichtenstein (1982) (10).

The foregoing cited studies have provided key information important in:

1. Predicting environmental impact of terminal residues.
2. Predicting field behavior from controlled laboratory studies.
3. Determination of extent of bound residues and binding capacity of soil.
4. Determining whether unique, toxicologically significant terminal residues are formed in the soil.
5. Assessing hazard of terminal residues by comparing their occurrence and magnitude in animals, plants, and soil.

The latter (i.e. 5.) is useful in situations where unusual degradation products can be identified in the soil. In such situations further toxicological studies may be needed to assess the potential hazard of terminal residues.

Predicting nonmetabolic disposition rates and routes for pesticides in the soil environment has been reported in this volume by other participants in the symposium. Our primary concern is with degradation associated with xenobiotic metabolism of microbial, fungal or exoenzymic origin.

The various factors governing degradation and dissipation of pesticides in soil can be identified as follows:

1. Chemical nature of the pesticide
2. Formulation and delivery system
3. Physical parameters - volatilization, sorption, leaching
4. Chemical parameters - hydrolysis, photolysis
5. Metabolism by microflora
6. Uptake by plants
7. Runoff in water or eroded soil
8. Edaphic parameters: soil type, pH, temperature, moisture

Of all parameters listed, degradation resulting from microorganismal metabolism is mostly responsible for dissipation of the parent pesticide in soil (11). Soil microflora account for less than 0.1% of soil by volume, yet population density reaches 10^9 ogranisms/g soil and fungal hyphae may reach several 1000 m/g soil and the biomass of microorganisms per hectare soil approaches several tons (11).

The major transformation reactions associated with microbial action in the soil are shown in Table 1. These reactions are largely of the same type involved in metabolism of xenobiotics in animals and plants (12). Generally these reactions include various hydrolyses, oxidations, reductions, desalkylation, decarboxylation and isomerizations. While in animals and plants these transformations facilitate further conversion into excretable or stored conjugates, these conjugation capacities are apparently lacking in soil microorganisms. However, metabolic capabilities of higher organisms are often modest by comparison with soil inhabiting heterotrophic bacteria and fungi (13). This can be illustrated by the ability of soil microorganisms to cleave aromatic rings via action of dioxygenases, eventually leading to total mineralization of aromatic xenobiotics (14). Indeed some aromatic herbicides are metabolized to compounds with functional substitutions such as: $-NH_2$, $-OH$, and $-COOH$. These products can be further incorporated by polymerization and esterification reactions into humic substances, thus remaining bound to components of the soil (15).

Metabolism of pesticides in the soil is also aided by cometabolism or cooxidation without concomitant, sustained growth of a microbial population which is growing on another substrate (16, 13). Golovleva *et. al.* (17) have demonstrated the foregoing cometabolism phenomenon in metabolic studies with the rice herbicide, molinate. The metabolism of molinate by *Mycococcus sp.* 104 was greatly accelerated in the presence of sucrose (0.1%) as a cosubstrate. Similarly, addition of ethanol (0.5%) accelerated the metabolism of molinate by *Pseudomonas sp.* 99. Further examples of microbial cometabolism of xenobiotics in the presence of various cosubstrates were given by Skryabin *et. al.* (18). As stated previously, the ability of soil microorganisms to metabolize xenobiotics in the soil is a major contributing

Table 1. Major Transformations of Pesticides in Soil

Reaction	Example
1. Hydrolysis	
Ester	Many
Amide	Propanil (Stam)
$C \equiv N \rightarrow CONH_2 \rightarrow COOH$	Fenvalerate
2. Oxidation	
Hydroxylation (Aliphatic, Aromatic)	Carbofuran
Epoxidation	Aldrin
$P=S \rightarrow P=O$	Parathion
Sulfoxidation	Phorate
3. Reduction	
$NO_2 \rightarrow NH_2$	Parathion
4. Involving Halogen	
$Cl \rightarrow OH$	Atrazine
$Cl \rightarrow H$	DDT, Lindane
Dehydrohalogenation	DDT
5. Dealkylation	
O -	Methoprene
N -	Trifluralin, Triazines
6. Isomerization Cis → Trans	Permethrin
7. Decarboxylation	Many

factor to reduction of the pesticide load in the environment. Several recent reports have shown that the soil microbial population can adapt and be induced to metabolize certain biodegradable pesticides at an accelerating rate, in some instances rendering the pesticide less useful.

Felsot et. al. (19) have reported evidence suggestive of an inductive selection process in Pseudomonas sp. in Illinois cornfields, resulting in accelerated degradation of the carbamate insecticide carbofuran and reduction in corn rootworm control. Reduced weed control in corn in certain soils in New Zealand was apparently due to accelerated microbial degradation of the herbicide EPTC plus antidote [Rahman et al., (20)]. Similar reports of accelerated degradation of EPTC plus an antidote (R-25788) in soil resulting in reduced weed control were attributed to microbial degradation in certain midwestern soils in the U.S. Degradation was retarded by coapplying an extender, Stauffer R-33865, which most likely inhibited microbial oxidation or hydrolysis of the thiocarbamate herbicide [Harvey and Schuman, (21); Gunsolus and Fawcett, (22)].

The U.S. Environmental Protection Agency (EPA) has recognized the importance of soil degradation studies as being highly important in incremental risk assessment associated with the registered use of pesticide chemicals. Relevant to this, the EPA has developed detailed guidelines for soil metabolism studies which are summarized in Table 2. These requirements are based on the Federal Insecticide, Fungicide, and Rodenticide Act as amended in 1972, 1975, 1978, and 1980, and on environmental chemistry guidelines issued by the EPA in 1975, 1978, and 1980.

Many of the required studies can be conducted in soil biometer flasks developed by Bartha and Pramer (1) and improved by Laskowski et. al. (23). An essential feature in these studies is the requirement for compound radiolabeling in one or more positions, usually using ^{14}C and occasionally ^{35}S, ^{32}P, ^{3}H and ^{36}Cl as a means of tracing the fate of the molecule and establishing a material radiobalance in the course of the study. Soil studies in biometer flasks should be conducted with fresh or "viable" soil to preserve microbial activity and soil structure. Under such conditions closer simulation of actual conditions may be achieved. Guth (8) has concluded from laboratory and field studies with 12 pesticides that no substantial differences existed in the pattern of metabolism of these compounds as a function of locale. However, the small number of published, comparative laboratory and field studies suggests that more research is needed in this area. Laboratory studies with a variety of soils has also established that soil type had minor impact on the metabolic pathway of pesticides studied (8).

To illustrate the major points discussed here as related to biodegradation of pesticides in soil, the following review of metabolism studies with several insecticides (fenitrothion, diflubenzuron and pyrethroids) and the herbicide molinate provides further details on these studies, their significance and environmental impact.

Table 2. Summary of U.S. EPA[1] Guidelines for Soil Metabolism Studies

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Aerobic Soil

Compound radiolabeled in one or more positions
Material balance; rate, type, and degree of metabolism
Identification of residues (more than 10% applied dose or 0.01 ppm)
Three or more soils for product with broad uses
Maintenance at 18-30°C and 75% of 0.33 bar moisture
Data collection until 90% loss of pesticide (up to 1 year)

Anaerobic Soil

Radiolabeled compound optional
Unnecessary if anaerobic aquatic metabolism study done
Pesticide first aged aerobically for 1 month
Anaerobicity (by water logging or purging with inert gas)

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[1] Extracted from: *Federal Register*, Monday July 10, 1978, Part II

FENITROTHION

A comprehensive laboratory study describing the degradation of the organophosphorus ester insecticide, fenitrothion, was reported by Spillner *et al.* (24), who studied its fate in two forest soils using [ring-^{14}C]-fenitrothion (20mCi/g). The methodology and results used in *this* study are described here as an illustrative model for metabolic fate studied in the soil. This compound has been extensively studied in plants, animals and components of the environment [Ohkawa *et al.* (25); Greenhalgh and Marshall (26); Miyamoto *et al.* (27); Takimoto and Miyamoto (28); Loos *et al.* (29)].

Studies reported here were conducted in two forest soils, an organic soil and a sandy loam whose physical properties were described in detail by Spillner *et al.* (24). The soils were evenly incorporated with 7.4 ppm [ring-^{14}C]fenitrothion as an emulsion and 50-g aliquots were placed in modified metabolism flasks described by Bartha and Pramer (1), and held at 30 ± 1°C for the duration of the experiment. The system has been designed for a total material balance study including provisions for monitoring of $^{14}CO_2$ and total CO_2. Soils were analyzed for fenitrothion degradation products periodically during the 56-day incubation period.

Soil microorganisms appear to play the key role in degradation of fenitrothion since over 90% of the applied dose was recovered intact after 30 days incubation in sterilized soils. In the viable soils degradation of fenitrothion was relatively rapid; the time for 90% degradation was 29 days in the organic soil and 15 days in the sandy loam. The proposed aerobic metabolic pathway for fenitrothion in both forest soils is shown in Figure 1.

Degradation products were identical in both soils. These were: 3-methyl-4-nitrophenol (MNP), 3-methyl-4-nitroanisole (MNA), CO_2 and a soil-bound fraction. Identity was established by two-dimensional, multiple cochromatography with authentic standards and by GC-coupled to a radioactivity monitor. A similar pattern of products was found in agricultural soils by Takimoto and Miyamoto (28) but reduced products such as aminofenitrothion, 3-methyl-4-aminophenol (MAP) and desmethyl-fenitrothion were detected in flooded soil (anaerobic) or from mixed culture isolates from soil (28).

The occurence of MNA (5% after 50 days incubation) in the soil is an unusual example of phenolic *O*-methylation in the soil. Previously Loos *et al*. (29) reported the methylation of 2,4-dichlorophenol to yield 2,4-dichloroanisole in *Athrobacter sp*. MNP is the major hydrolytic product of fenitrothion. It is rapidly formed at alkaline pH's and by action of esterases, most likely arylesterases of group II (30). MNP accounted for a high value of 40% of applied ^{14}C in sandy loam soil and 32% in organic soil 8 days after treatment.

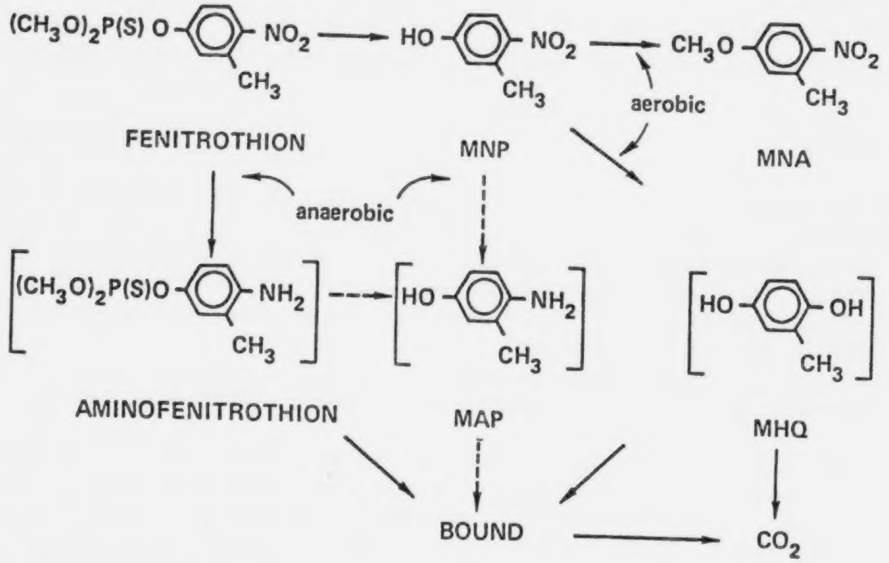


Figure 1. Aerobic and anaerobic metabolic pathway of fenitrothion in forest soils. From Spillner *et. al*. (24). Reprinted with permission from ref. 24. Copyright 1982 American Chemical Society

The transient occurrence of 2-methylhydroquinone (MHQ) is implied since it is a possible precursor to the formation of $^{14}CO_2$ which results from complete degradation of the phenyl ring. Very likely MHQ undergoes additional oxidation of the methyl group, followed by ortho ring scission and evolution of CO_2. The latter is also a major metabolic product as shown in Fig. 1. By analogy hydroquinone (HQ) has been observed in microbial degradation of phenolic soil residues leading to evolution of CO_2 as the terminal residue of aromatic ring cleavage by microorganisms (24).

The bound fraction represents a major proportion of the radiocarbon in the treated soil; 30-44% was incorporated into humic acid, 12-34% into fulvic acid, 20-29% was incorporated into a more insoluble fraction remaining after alkaline extraction, and 10-12% into organosoluble acidic compounds isolated from the fulvic acid fraction. Considering the mechanism of binding under aerobic conditions, MHQ is suggested as the precursor leading to binding. Most likely, MHQ polymerizes via free radicals which readily lead to binding to humic substances (24). Under anaerobic conditions the reduced (amino moiety) products of fenitrothion, in part, bind to the soil-bound fraction; by analogy, Katan et al. (31) and Katan and Lichtenstein (32) reported similar findings involving reductive soil degradation of parathion.

Neither fenitrothion nor its identified metabolites MNP and MNA had an observable detrimental effect on soil bacteria, actinomycetes, fungi and yeasts as determined by CO_2 evolution (respiration) and plate counting techniques at the elevated treatment rate described in the foregoing study.

The degradation curves of fenitrothion in an organic soil (OS) and a sandy loam soil (SL) (Fig. 2) were calculated using data generated in the study by Spillner et. al. (24) and from the two-compartment model derived by Hamaker and Goring (33) for pesticide degradation in soil.

In this model (Fig. 2) K is the degradation rate constant; K_1 the rate constant describing the transport of the pesticide from the labile to the unavailable compartment; and K_{-1} the rate constant for transport of pesticide from the unavailable to the labile compartment. The total observed concentration of the parent compound obtained through extraction and analysis is $C = C_1 + C_2$, where C_1 and C_2 denote the concentration of the pesticide in the labile and unavailable compartments, respectively. The differential equations which describe degradation of the pesticide are:

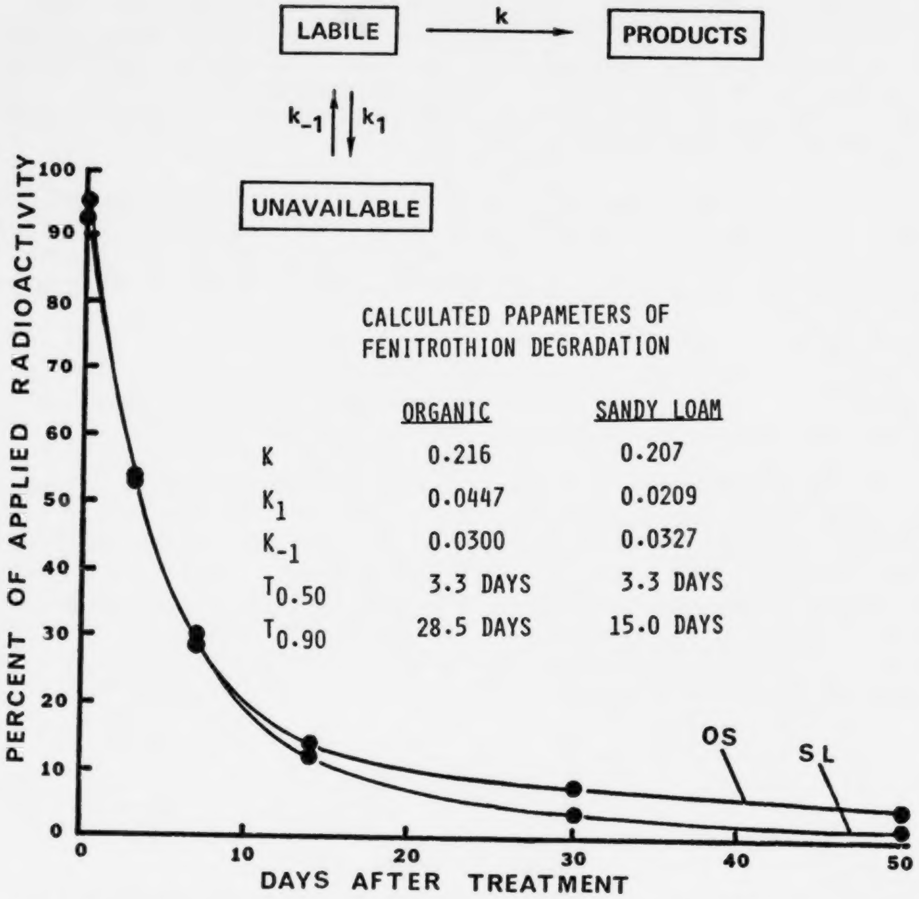
$$-\frac{dc_1}{dt} = (k + k_1)c_1 - k_{-1}c_2$$

$$-\frac{dc_2}{dt} = k_{-1}c_2 - k_1c_1$$

The K values are similar for both soils (Fig. 2). This suggests that soil type is not a major critical factor governing degradation, a finding in concert with the conclusions reached by Guth (8). The time for 90% degradation ($T_{0.90}$) was reached faster in SL than in OS, most likely due to contribution of K_1. The degradation rate for fenithrothion in both forest soils was faster than that reported in agricultural soils. The faster rate could have resulted from the higher temperature at which this study was conducted (24).

DIFLUBENZURON

The chlorophenylbenzoyl urea insecticide, diflubenzuron, represents a novel insecticidal mode of action by virtue of inhibiting chitin deposition, and having ovicidal and chemosterilant action in important target insects. Furthermore it belongs to a chemical class which was not previously studied in the soil, and other components of the environment.



CALCULATED PAPAMETERS OF
FENITROTHION DEGRADATION

	ORGANIC	SANDY LOAM
K	0.216	0.207
K_1	0.0447	0.0209
K_{-1}	0.0300	0.0327
$T_{0.50}$	3.3 DAYS	3.3 DAYS
$T_{0.90}$	28.5 DAYS	15.0 DAYS

Figure 2. Degradation of fenitrothion in organic soil (OS) and sandy loam (SL) and calculated parameters of degradation based on a two-compartmental model for pesticides degradation in soil. Adapted from Spillner _et_. _al_. (24).

The metabolic and degradative fate of diflubenzuron has been reviewed by Hammock and Quistad (34). The importance of formulation and physical state of the chemical and delivery was indicated by Verloop and Ferrell (35). The authors noted that particle size was a key to the longevity of the compound in soil. The half-life was reduced from 16 weeks to one week with reduction of particle size from 10 microns to 2 microns. Apparently the half-life is governed by the rate of dissolution, K_1, or by the true rate of degradation, K_2. Apparently K_1 is rate determining because the shorter half-life with smaller particle size approximates the disappearance rate of the compound when present in true solution (35).

$$\text{Diflubenzuron suspension} \xrightarrow{K_1} \text{diflubenzuron solution} \xrightarrow{K_2} \text{metabolites.}$$

In contrast, soil type had much less influence on the rate of degradation, similar to the findings of Spillner et al. (24). In five agricultural soils and three hydro soils, the range in half-lives was only two-fold.

The importance of microbial degradation was also reported by these authors using [^{14}C-anilino]diflubenzuron applied at field rates to steam-sterilized and viable sandy-loam soil. In the viable soil only 2% of the parent compound remained whereas 94% of parent was recovered from the sterile soil, thus indicating the importance of microorganisms in transforming this compound in the soil environment.

The metabolic pathways of diflubenzuron in soil and their interrelation to movement and transformation in plants and animal, is shown in Figure 3, courtesy of Dr. G. G. Still, USDA, Washington, D.C. (1981). Primary degradation in soil resulted from hydrolysis releasing p-chlorophenylurea as the major product (20% of applied ^{14}C after two weeks) and 2,6-difluorobenzoic acid. Bound residues arise from binding via the amino moiety of p-chlorophenylurea; only small amounts of free p-chloroaniline were found from the phenylurea precursor in soil.

Using the parent compound, independently labeled with ^{14}C in the carbonyl group of the benzoyl ring or ^{3}H in the ring, it was shown that 2,6-difluorobenzoic acid was also a major metabolite with maximum concentrations reaching 20% of the applied dose and a half-life of less than four weeks. Further transformation led to decarboxylation of the benzoic acid, releasing a major portion of the ^{14}C as $^{14}CO_2$. A minor route of soil metabolism cleaves the parent compound, releasing small amounts of p-chloraniline which was present in the bound residue.

Figure 3 summarizes the metabolism and degradation of diflubenzuron in plants, soil and animals. It is interesting to note that while diflubenzuron undergoes amidolysis and decarboxylation reactions leading to numerous degradation products in the soil, several researchers have demonstrated the refractory nature to metabolism of the parent compound when deposited on plant surfaces. The compound is not systemic and dissipates largely unchanged from plant surfaces with minor intervention due to photodegradation (35).

Mansager et al. (36) have also shown the refractory nature of diflubenzuron on and in cotton plants grown in soil treated with [^{14}C]-diflubenzuron labeled in both phenyl moieties. Only traces of ^{14}C-labeled chlorophenylurea were recovered from foliar tissue while root tissues contained trace amounts of the parent compound and 2,6-difluorobenzoic acid.

Similar metabolites to those isolated from soil were identified in urine and feces of rats orally dosed with [^{3}H-benzoyl] and [^{14}C-anilino]-diflubenzuron. In addition to 2,6-difluorobenzoic acid and p-chlorophenyl urea (20% of recovered dose), major transformation reactions involved ring hydroxylations of the intact parent molecule (80% of recovered dose) as shown in Figure 3.

The three compartment physical model shown in Figure 3 demonstrates the key role the soil plays in degradation of what otherwise might have been a persistent pesticide. Furthermore soil microorganisms not only approximate the action of liver microsomal enzymes, but often have greater capacity than liver enzymes in their metabolic capacity, in transforming xenobiotics to CO_2 and to formation of various biopolymers.

MOLINATE

Fenitrothion and diflubenzuron represent pesticides reaching the soil milieu as unintentional contaminants. Preemergent herbicides represent a class of pesticides which are applied directly and intentionally to the soil. An appropriate example in this category is the selective thiocarbamate herbicide, molinate, which has been extensively used in the USA, Japan, USSR and throughout the rice growing regions of the world for control of barnyard grass, Echinocloa sp., in rice culture. The use of this herbicide in rice culture makes it an ideal model compound for studying its impact and degradation in various components of the environment. The metabolism and degradation of molinate have been studied extensively in rats by DeBaun et al. (37), in fish by Lay et al. (38) and by Lay and Menn, (39), in microorganisms by Golovleva et al., (17), in rice fields by Soderquist et al. (40), and in the soil by Thomas and Holt (41).

Thomas and Holt (41) have shown in controlled laboratory studies with [ring-^{14}C]molinate (8.2 mCi/mmol) that 50% of the applied dose was lost after three weeks under aerobic conditions, while under anaerobic (flooded) conditions a loss of 50% of the applied dose was encountered after 10 weeks. Under anaerobic conditions little degradation of molinate occurred and volatilization was the prime route of dissipation. Soderquist et al. (40) have determined that under actual field conditions volatilization accounted for 75-85% loss of molinate from the water phase of the treated rice field within 48 hours after treatment. These researchers have also shown that photolysis provided only a minor contribution to the degradation of molinate. This is probably due to the absence of a significant chromophore in the molecule and consequently molinate does not absorb appreciable solar energy (42). However, certain pesticides can be degraded more rapidly under anaerobic conditions. Sethunathan (43) reported that in flooded soils the insecticides δ-BHC, methoxychlor, DDT, heptachlor, endrin, parathion and diazinon were degraded significantly more rapidly than under aerobic conditions. The rapid degradation under the anaerobic conditions is most likely due to metabolism by anaerobic soil microorganisms. The predominant reductive transformation reactions involving these pesticides have been listed in Table 1.

Thomas and Holt (41) reported that under aerobic conditions, 32 weeks after treatment, 30% of the applied [^{14}C]molinate was present in the bound fraction and only approximately 5% in the organosoluble fraction.

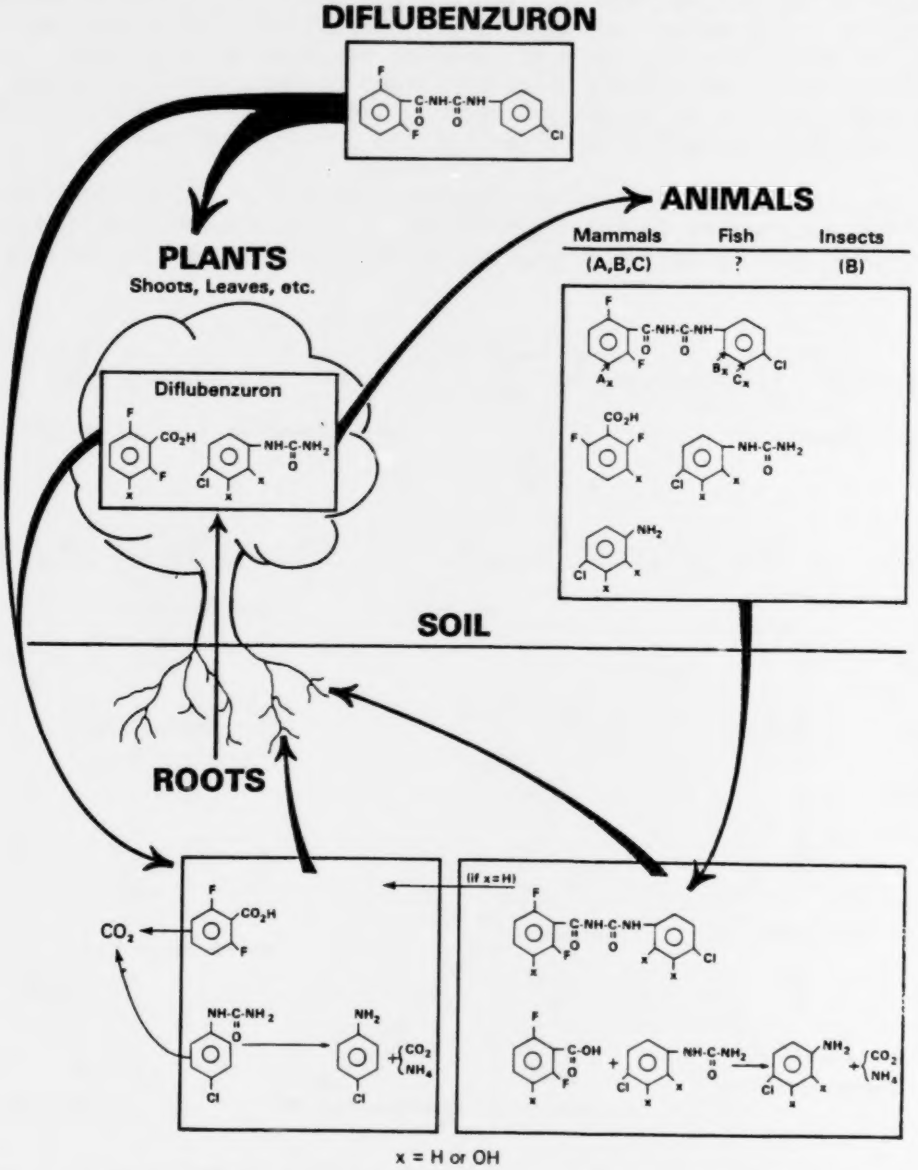

DIFLUBENZURON
PLANTS
Shoots, Leaves, etc.
Diflubenzuron
ANIMALS
Mammals
Fish
Insects
(A,B,C)
?
(B)
SOIL
ROOTS
CO₂
(if x = H)
x = H or OH

Figure 3. Comparative aspects of metabolism of diflubenzuron in soil, plants, and animals. Courtesy of G. G. Still, 1981.

In the latter fraction approximately one half of the radiocarbon was recovered as the parent compound and the remaining radiocarbon was distributed among the metabolites shown in Figure 4. The pathway incorporates the comparative metabolic routes of molinate in soil under aerobic conditions, metabolism in fish, the rat, and its photolytic degradation products.

Comparing the soil degradative products with those identified in rat urine (37) reveals that major biotransformation in the rat involves sulfoxidation and conjugation with glututhione (GSH), resulting in molinate mercapturate as the major terminal urinary metabolite. Other terminal products of metabolism involve O-glucuronide conjugation of 3- and 4-hydroxymolinate. Hydrolysis of sulfoxidized molinate and its hydroxy derivatives gave rise to hexamethyleneimine (HMI) and 3- and 4-hydroxy-HMI; these metabolites accounted for 87.4% of the urinary radiocarbon.

In the soil neither GSH conjugation nor conjugation of the hydroxylated species was observed by Thomas and Holt (41). Identified metabolites in the soil included hydroxylated molinate and its keto derivative, acetylated

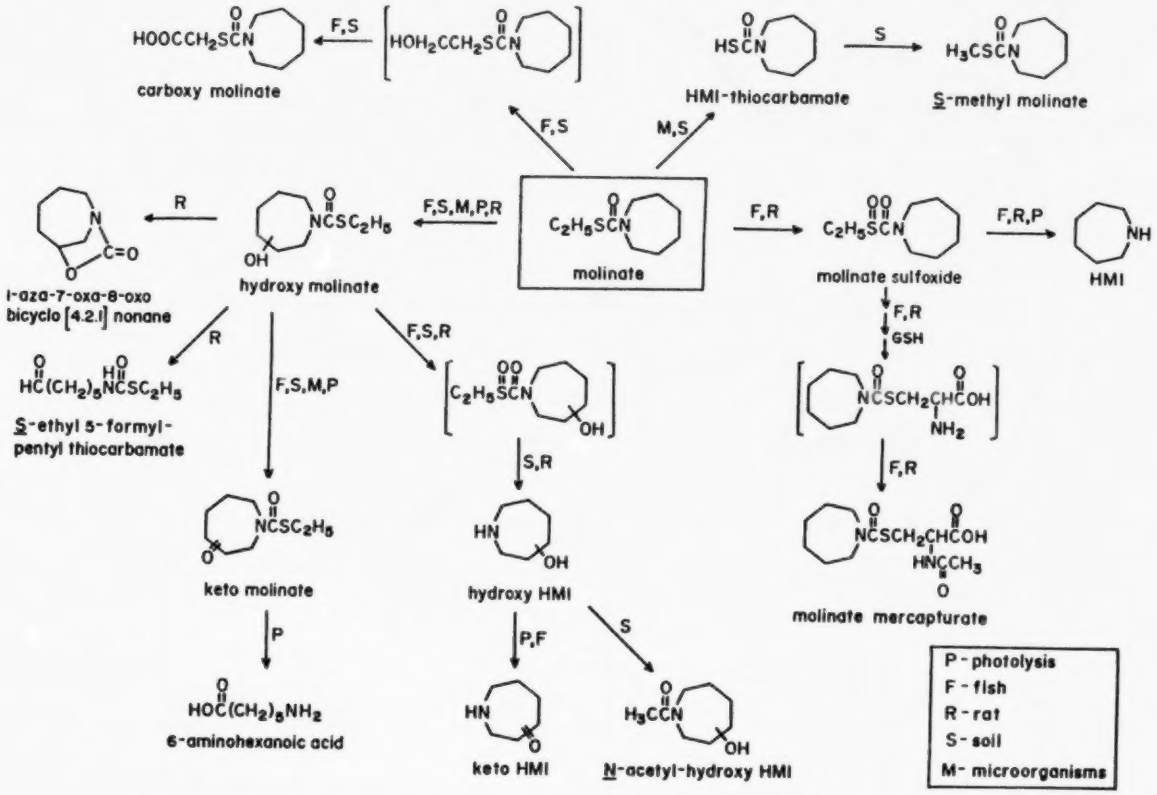

carboxy molinate
F,S
HMI-thiocarbamate
S
S-methyl molinate
F,S
M,S
R
F,S,M,P,R
molinate
F,R
molinate sulfoxide
F,R,P
HMI
1-aza-7-oxa-8-oxo bicyclo [4.2.1] nonane
hydroxy molinate
R
F,S,M,P
F,S,R
F,R
GSH
S-ethyl 5-formyl-pentyl thiocarbamate
S,R
F,R
keto molinate
hydroxy HMI
molinate mercapturate
P
P,F
S
6-aminohexanoic acid
keto HMI
N-acetyl-hydroxy HMI
P - photolysis
F - fish
R - rat
S - soil
M - microorganisms

Figure 4. Comparative metabolic pathway of molinate in the rat, fish, soil and its photolysis products. (Based on: DeBaun et. al., (31); Lay et. al., (38); Lay and Menn, (39); and Thomas and Holt, (41).

hydroxy- HMI and HMI. An unusual metabolite involved desethylation of molinate followed by 3-methylation giving rise to S-methyl-molinate. Another minor pathway involved formation of carboxymethyl-molinate, also observed in fish by Lay, et al. (38).

Golovleva et al. (17), studying the metabolism of molinate in enriched microorganism cultures, have also identified 2-hydroxy- and 2-keto-molinate and the desethylated thiocarbamic acid derivative as terminal degradation products formed by Mycococcus sp. 22P.

Fish represent the apex of the ecological biomagnification chain in the hydrosoil environment. Metabolism studies of [^{14}C]-molinate in the living Japanese carp, Cyprinus carpio var. Yamato Koi, have shown that molinate is extensively metabolized in the fish giving rise to terminal metabolites (38) which were also identified in the rat and to a large extent by soil microorganisms. These included molinate sulfoxide, ring-hydroxylated molinate, isomers of keto molinate, keto-HMI, and HMI. These studies confirmed for the first time the formation of molinate mercapturate resulting from GSH conjugation in the carp (39).

The molinate degradation and dissipation model outlines the results of the action and interaction of many of the key biotic and abiotic forces which govern the rate of persistence of a xenobiotic compound in the soil and soil/water compartments of the environment. Furthermore the foregoing studies provide useful data in forecasting the environmental behavior of molinate and other similar compounds under various edaphic and climatic conditions.

SYNTHETIC PYRETHROIDS

The photostable synthetic pyrethroid insecticides are a remarkable new class of potent insecticides (44). These compounds are active at remarkably low concentrations against a broad spectrum of insects. Kaufman et al. (45) have shown that permethrin was rapidly degraded in soil with a major contribution from soil microorganisms. Primary degradative attack resulted in ester hydrolysis giving rise to 3-(2,2-dichloroethenyl)-2, 2-dimethylcyclopropanecarboxylic acid (DCVA) and 3-phenoxybenzyl alcohol (PBA). Hydrolysis of the ester bond was also the major transformation step in soil degradation of cypermethrin (46); fenpropathrin (47) and fenvalerate (48). PBA, the alcohol hydrolysis cleavage product of permethrin, undergoes further microbial oxidation in the soil to 3-phenoxybenzoic acid [Kaufman et al., (49)].

Using soil columns for leaching experiments and soil thin-layer chromatography for determination of mobility of ^{14}C-labeled pyrethroids (permethrin, decamethrin and cypermethrin) in three diverse soil types, Kaufman et al. (45) showed virtual immobility in soil and the parent pyrethroids could not be leached through the soil, although the alcohol (PBA) and acid (DCVA) hydrolysis products showed low soil mobility. Based on these model studies the investigators concluded that these pyrethoids pose no soil transport hazard to the environment.

Soil metabolism studies were conducted in our laboratory with the synthetic pyrethroid, fluvalinate (50). These studies were conducted in biometer flasks containing 100 g keaton sandy loam treated at rate of 0.11 kg/ha with [CF_3-^{14}C]fluvalinate. The aerobic incubation system was designed according to Laskowski et al. (23).

Under these conditions the time for 50% degradation of fluvalinate was approximately six days. Eight weeks after treatment the principal soil residues were fluvalinate (11% of applied dose), the haloanilino acid from ester hydrolysis (8%), and 2-chloro-4-trifluoromethylaniline (9%). The latter volatilized rapidly from soil (41% of applied dose). A second major volatile product was $^{14}CO_2$ (9%) resulting from degradation of the $^{14}CF_3$ moiety. The metabolic pathway of fluvalinate in soil is outlined in Figure 5. Fluvalinate and its principal metabolites were not translocated into growing crops such as lettuce, radishes and wheat planted in soil 31 days after treatment with [^{14}C]fluvalinate. Since the synthetic pyrethroids are inactive as soil insecticides, reaching the soil only as unintentional contaminants where they are readily metabolized and in some instances volatilized, they are among the least likely pesticides to contaminate the soil environment.

CONCLUSIONS

While progress has been made in recognizing the soil as the major compartment for transformation and degradation of pesticides in the environment, much additional research is needed in the following areas to obtain a better understanding of the processes involved in the routes and rates of pesticide dissipation in and from the soil:

1. Significance and identity of soil-bound residues.
2. Mechanisms of adsorption and desorption.
3. Effect of chemical interaction in soil on metabolic fate of each component chemical.
4. Microbial adaptation, enzyme induction, and the role of plasmids in soil microorganisms.
5. Standardization of methods to determine biological activity of test soils.
6. Effects of no- and low- till farming on fate and residues of pesticides in the soil.
7. Application of mathematical modeling to prediction of fate and kinetics of persistance of terminal pesticide metabolites in the soil environment.

It is anticipated that the joint U.S./U.S.S.R. project will place considerable effort in conducting research in these areas with special emphasis on item number 7.

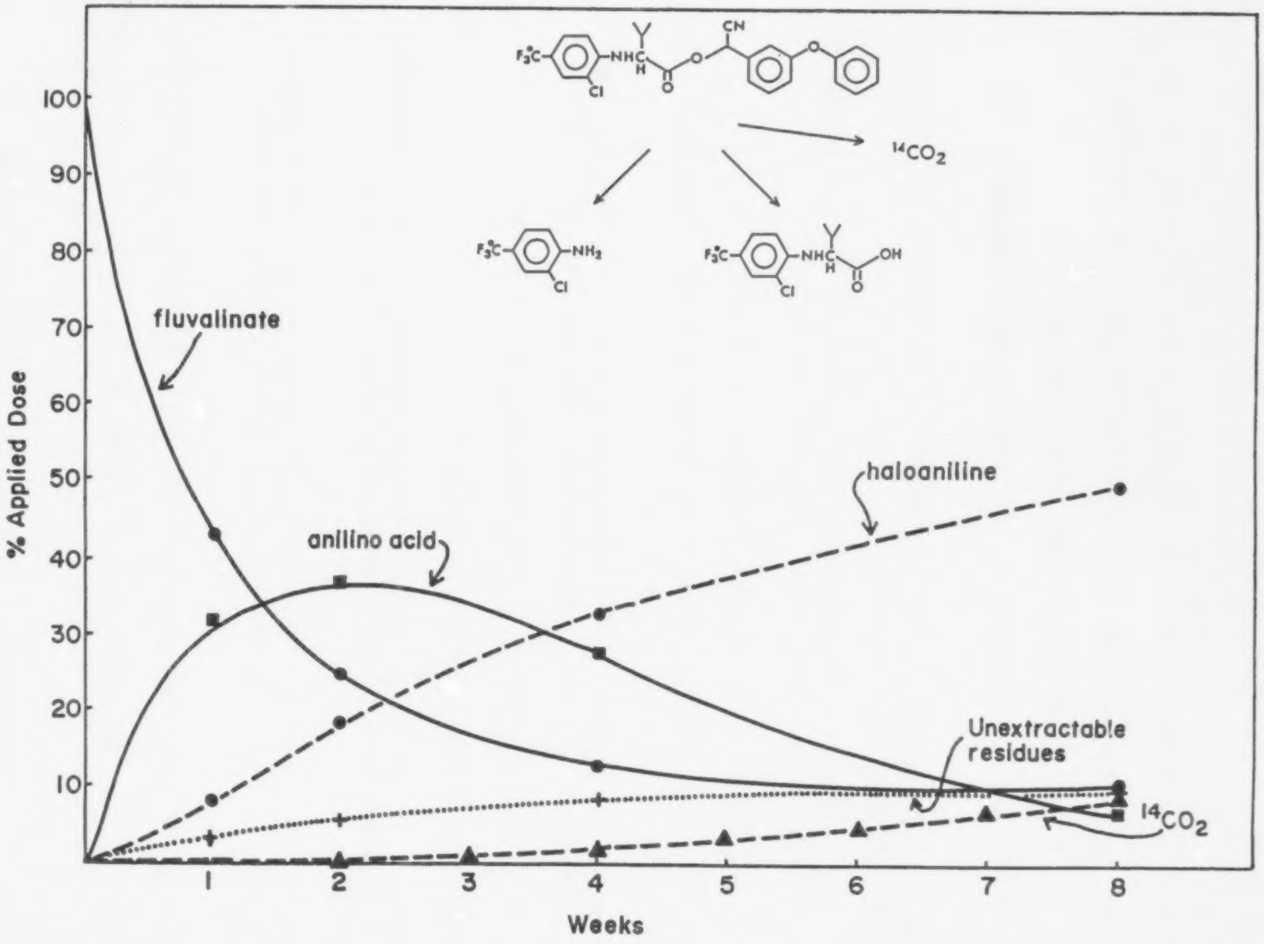


Figure 5. Degradation of fluvalinate in sandy loam soil after treatment at 0.1 kg/ha.

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ON THE POSSIBILITY OF PREDICTING PESTICIDE BEHAVIOR IN SOIL

by

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ABSTRACT

Pesticide degradation in soil depends not only on the chemical structure and partition coefficient in the system "soil/soil solution" but also on the ecological conditions determining the activity of specific soil microorganisms. Some reference data discussed in the paper, concern the relationship between the rate of degradation, migration capacity, and other characteristics. Pesticide degradation in soil is shown to be controled by main, additional and indifferent factors, that are all presented. Major mathematical models describing the process are considered in brief. Particular attention is given to the conceptual model by Fumidge and Osgerby (1967) describing migration and degradation in soil of pesticides and other xenobiotics, and having certain advantages.

Almost any soil can be viewed as a heterogeneous system comprising four phases: solid (a soil matrix), liquid (soil solution), gaseous (soil air), and living matter (soil biota). Pesticides may be present in soil in three forms: as a solution, in an immobilized (absorbed, sorbed) state, and in a vapor form. These forms maintain a dynamic equilibrium which can be tipped off when certain factors are changed, particularly temperature and moisture content. As pesticides are, as a rule, characterized by moderate or low volatility, major interest of a researcher studying their persistence in soil, is concentrated at that part of the compound which occurs in a dissolved form or in an immobilized state. The compound partition coefficient in the system soil solid phase/soil solution corrected for humus content is likely to characterize adequately the pesticide sorption by a group of genetically similar soils.

The task of predicting the dynamics of pesticide content in soil can be simplified by the introduction of the following:

- the removal of pesticide residues with solid and liquid runoff from the soil arable layer can be ignored, as well as the chemical loss due to volatilization, photodegradation and removal with the phytomass;
- we assume that biological and chemical transformation and decomposition affect only that part of the pesticide which occurs in soil in a dissolved unsorbed form (I4).

This approach permits the researcner to bring multivariant processes of pesticide transformation and degradation in soil to the analogous processes occurring in water in the system bottom sediment/water.

A supposition that a sorbed pesticide is not available to microorganisms even in the culture medium or a pure microbial culture is confirmed by our data on propanil sorbed by montmorillonite (2,3), and by the data of the US scientists on n-decylamine (28).

And finally, while predicting the duration period of pesticide persistence in soil a researcher has to make one more assumption, namely, that in the dozes recommended for application the chemical will not inhibit soil biota or its functions.

Thus, the decomposition in soil of a natural compound or a xenobiotic is determined by the following groups of factors:

a) chemical structure of the compound;
b) physico-chemical form of the compound in soil, and
c) ecological conditions directly or indirectly affecting the pesticide biotransformation and biodegradation in soil.

Group of factors (a) includes the data on the compound physico-chemical and chemical properties. In the opinion of G.G. Briggs (9) this is sufficient for making a conclusion on the persistence of a pesticide in soil. He believes that the partition coefficient in the system of two immiscible liquids (P) or in the system soil/water (K_p) is the determining characteristic. In the latter case K_p is corrected for the organic matter content in soil. The value of K_p characterizes an available (actual) part of the compound present in the soil liquid phase (soil solution). According to availability value (A), Briggs assigns all pesticides to 14 classes. Class 1 comprises compounds the concentration of which in solution is more than 75% (high availability) of their total content in soil. Class 14 comprises pesticides with a solution concentration less than 0.01% (low availability). Very mobile compounds have availability 1-2, and practically immobile,(7-14). The author also introduces the value of degradability (D). This suggests, attributively to the molecules of independent organic substances, the following assumptions.

- Each functional group in a molecule can be transformed in a specific manner.

- The most labile groups in a polyfunctional molecule will be transformed most rapidly.
- Variation of degradability of similar functional groups in a pesticide molecule is determined by their position as well as by steric and electron effects.
- And finally, the metabolite degradability is determined by the properties of new functional groups formed in a pesticide molecule in the process of metabolism.

Knowing the pathways and rate constants of chemical and enzymatic transformations of compounds, Briggs groups pesticides, according to their degradability, within a 1-10 scale depending on the presence in their molecule of certain functional groups. Using the product of the compound "availability class" (A) and degradability (D), Briggs calculates the half lives of various groups of pesticides.

The data on organophosphorus compounds and organochlorine insecticides (12) illustrate the validity of this approach. Using the data of some other authors, Briggs establishes a very good reverse relationship between degradability and migration capacity of 65 pesticides.

Unlike the mentioned approach of Briggs, an attempt made by the authors (8) to predict pesticide persistence in the environment on the basis of only the compound chemical structure seems to us less successful. In their calculations, these authors used the bank of reference data on the rate of degradation of several chemicals in soil. However, they did not use K_p, ignored specific soil conditions and that is probably the reason for a very wide range of the degradation rate variations they got.

The factors of group (b) include first of all such representative values as the compound partition coefficient in the system of immiscible liquids (P) and in the system sorbent/solution (K_p). Compulsory studies of the process of sorption to understand the fate of chemical in soil and to define the share of the immobilized compound are examined in detail elsewhere.

The factors of group (c) affecting transformation and degradation of a pesticide in soil are divided on the basis of reference data and the results of our experiments into main (temperature and moisture content of soil), additional (organic fertilizer, aeration, soil pH, soil mineralogical and mechanical composition, content and fraction composition of humus, cultivated crop and agricultural technology), and indifferent (content of NPK, micronutrients, salts, composition absorbed cations). As only few of the main and additional factors can be controled in the open agroecosystems, the potentialities of artificial control of the degradation rate of pesticides in soil are very limited.

During the last two decades a large number of various empirical and semi-empirical equations have been suggested. Using these equations and individual parameters of one or several groups of factors (a)-(c), the authors calculated the rate of degradation and the residual content of pesticides in soil. However, we do not know yet of any mathematical models which describe biodegradation of herbicides or other pesticides in soil and take into account a combined action of main and additional factors on their degradation. The only exception is simulative mathematical models of Walker (23-26) simultaneously considering varying values of soil temperature and moisture content, ant their various combinations.

The most numerous group of mathematical models can be reduced to various equations of linear regression. They are considered in detail in a review paper by Hamaker (I5). We shall discuss only some basic principles.

Models describing pesticide degradation in soil are given for a number of compounds: bromacil (27), picloram (20,I3), 2,4-D (4), carbaryl (6), propyzamide (I9,26), and napropamid (2I). However, all these models based on linear regression equations suffer a common drawback: they are limited, take into account only some randomly picked factors (humus, pH, mechanical composition), and ignore climatic conditions (temperature, humidity, insolation).

To describe pesticide kinetics in soil a first-order reaction equation is widely used giving an exponential function:

$$C_t = C_0 e^{-kt}, \qquad [I]$$

where k is the empirical degradation rate constant; C_o and C_t are the initial and the time-determined (t) concentrations of a toxicant in mg/kg, respectively.

Thus, according to the conceptual model of Furmidge and Osgerby (I4) pesticide degradation in soil occurs according to the first-order kinetics, and actually only the portion of pesticide dissolved in soil solution degrades. The degradation rate (dc/dt) in soil is calculated by the following equation:

$$dc/dt = \frac{-kc}{1+M_s/M_w K_p}, \qquad [2]$$

where K_p is the partition coefficient of chemical in the system soil/soil solution;
M_s and M_w are the masses of soil solid and liquid phases in the systems, respectively.

Formula [I] can be considered one of the possible empirical functions, rather than a consequence of a sufficiently complete mathematical model characterizing specific features of pesticide disappearance from soil. This expression includes only one parameter (k) characterizing the pesticide degradation conditions. It is assumed that these conditions remain inchanged during the whole period of exposure and that the process rate does not depend on C_o (5).

In fact, as it was obseved in the experiment on picloram (I6), the relative degradation rate in several US and Canadian soils, i.e. T_{50} and T_{99}, depended on the initial concentration of the chemical (C_o). At lower concentration in soil, degradation rate increased. Analogous facts were observed for propanil (I0), linuron (7) and 3,4-DCA (I8). In our experiments, propanil (10, 50 and 250 mg/kg) showed reliable differences in the T_{50} value between the minimum (average) and maximum concentrations. 3,4-DCA gave reliable differences in the T_{50} value among all the three concentrations. A change (slowing down) in the degradation rate is apparently a response of soil microorganisms and testifies to a marginal state of the soil self-cleansing capacity relative to the introduced toxicant.

So, even if the pesticide degradation in soil is described exponentially, the researcher has to calculate value k at least for the cases where the doses of one and the same chemical differ sharply.

Several authors (II ,I5, I7) stress the point that various processes largely affect the content and form of a chemical in soil in the initial period immediately after its application. In case of surface application this initial loss may constitute up to 30% (22).

Disking in of a chemical in soil immediately after its application significantly accelerates the process of its redistribution within the soil layer and reduces the time needed for the system soil/herbicide to reach equilibrium(15).In our field experiment on linuron (5) in the soddy-pale-podzolic soil the loss of the chemical was approximately 20% quicker if the herbicide (0.5 kg/ha) was applied on the surface as compared to disking in the 0-5-7 cm layer. This loss rate can be explained by photodegradation and volatilization of linuron when it was on the soil surface. Consequently, to increase the pesticide effect or to reduce its effective dose where it is agrotechnically permissible, it seems advisable to disk the chemical in the top soil layer immediately after application.

Hamaker (I5) divides all disappearance curves of pesticides in soil into three classes (based on the shape of curve when plotted on semilog axes):

1) concave upward;
2) concave downward (characteristic also of the case where degradation occurs after a lag-period);
3) a straight line (i.e., first-order).

The first class is much more common, particularly for describing the degradation dynamics of a chemical under field conditions. That indicates a limited application of the first order kinetics equation.

To assess quantitatively the experimental results on pesticide degradation in soil we used the following expression (6) for a portion of chemical y(%) degraded in time t_y:

$$y = \Phi\left(b \lg \frac{t_y}{T_{50}}\right) \cdot 100\,\% , \qquad [3]$$

and with the lag period

$$y = \Phi\left(b \lg \frac{t_y - T_{LAG}}{T_{50} - T_{LAG}}\right) \cdot 100\,\% , \qquad [4]$$

where

$$\Phi(x) = \frac{1}{\sqrt{2\pi}} \cdot \int_{-\infty}^{x} e^{\frac{-x^2}{2}} dx$$

Formula [4] unlike the exponent, describes more adequately the dynamics curves for all the three groups characterizing the degradation of herbicides and their transformation products in soil.

Based on formulae [3] and [4] , we suggested a method for predicting the dynamics of organic pesticide content in soil that is currently being tested under field conditions. The main point of the method is that parameters T_{50}, T_{LAG} and b are determined at definite values of main and additional factors in the course of model experiments under "standard soil conditions". Testing showed that the estimated and experimental data for different soils lie within 1-33% (1,5).

We believe that for predicting the pesticide dynamics under field conditions it is necessary to determine most accurately its initial concentration after application (introduction into soil) and to record daily average temperature during the exposure period, provided the temperature range stays within the biological minimum. As in this case only actual degradation of a chemical is determined, while the disappearance factors associated with removal, evaporation, photolysis and other losses, are ignored, the residue persistence will be somewhat overestimated. However, this is not a disadvantage when similar results are used for regulating application doses and residues of a chemical in soil, because any recommendations must have a certain "reserve coefficient".

Not wishing to set this approach against other methods for predicting the soil dynamics of herbicides or other pesticides we may list as its advantages the accessible and simple technical procedure, satisfactory reproducibility and the opportunity to create a data bank for different chemicals, soil types and ecofactors to be repeatedly utilized. It is also important that experimental data can be obtained in any season that is of great use for the toxicologists of agrochemical laboratories in "Soyuzselkhozkhimiya" - they have very limited resources for arranging any extra studies during the growing season. This approach will also allow to improve the accuracy of prediction of soil selfcleansing from pesticides under extreme conditions, e.g. in case of accidental soil pollution with a considerable amount of chemicals caused by overdosing, emergency, etc. Any mathematical model is believed to be adequate provided theoretical and experimental data agree well. Otherwise, the process of pesticide degradation in soil is obviously affected by factors missed in the model. That happens more often when the models are developed a priori. The objective of those working in the area is to develop sufficiently reliable methods capable of extrapolating laboratory data to field conditions.

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FORECASTING PESTICIDE MOBILITY IN SOILS:

DISPERSION AND ADSORPTION CONSIDERATIONS

by

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ABSTRACT

Mathematical models of pesticide movement in soils can serve two principal purposes: (a) quantitative evaluation of the dynamics of various key processes (and their interactions) which control pesticide mobility, and (b) prediction of the leaching and distribution of pesticides in field soils for various combinations of pesticides, soils, water-flow regimes and environmental conditions of practical interest. Considerable progress has been made in modeling transport processes for well-defined systems such as laboratory columns of sieved soil, but accurate field-scale predictions are generally still beyond our technical grasp. Comprehensive models should include mathematical descriptions of pesticide sorption, dispersion, transformation, volatilization and plant uptake. This paper focuses principally on the interaction of sorption and dispersion processes and on laboratory assessment of sorption for prediction of pesticide mobility in field soils. Currently available sorption methodology is probably adequate for many applications, but improved methods of determining dispersion coefficients for field soils are needed. Useful field predictions are hindered by inadequate characterizations of (a) water flow through large pores or fractures and the consequent lack of equilibrium between adsorbed pesticides and new additions of water, (b) the apparent increase in adsorption over prolonged periods of time, especially in surface soils with relatively high organic matter content, and (c) apparent non-singularity in the adsorption-desorption process for certain pesticide-soil combinations. Future research on these processes and their interactions with volatilization and transformation will depend on the exactness required of predictions. Simple convection-type models using conventional batch-suspension adsorption data may suffice for many field applications, while other situations will require more exact mathematical representations of real processes. Finally,

the successful use of mathematical models to forecast pesticide mobility in field soils will require reliable prediction of water flux in the soil profile and also characterization of spatial variability of soil hydraulic properties and of adsorption and dispersion.

INTRODUCTION -- A PERSPECTIVE ON MODELING PESTICIDE MOVEMENT

Though I am somewhat uncomfortable with the word "forecasting" in the title of this paper, I think "forecasting" probably conveys two important ideas about our subject. First, we are interested in determining in advance the outcome of a pesticide practice under a given set of conditions, with respect to the agricultural efficacy of the practice and also relative to environmental quality. And second, there is a measure of uncertainty in predicting pesticide movement on a field scale. Forecasting pesticide movement in soils is somewhat analogous to weather forecasting. Weather forecasts are extremely important to agriculture in most parts of the world and mathematical modeling has contributed substantially to weather forecasting for over three decades, yet weather forecasting is still far from exact. Such are the short-term prospects for forecasting the field movement of many pesticides under a variety of soil-climate-crop management regimes.

Pesticides, as a group of chemicals, include compounds which vary widely in their water solubility, volatility, persistence in the soil environment and adsorption on soil colloids. The soils to which pesticides are applied (whether intentionally or by accident) are also highly variable, in their chemical, mineralogical, physical and biological properties. Also, soils may not be homogeneous and isotropic, on the scale of interest to us, as the assumptions for mathematical analysis frequently require. But despite the difficulties of adequately representing a host of processes and their interactions by mathematical equations, the alternative methods of assessing the environmental risk of using a pesticide are generally less attractive. Studies of individual processes in physical models are informative, but interactions between processes (e.g. between volatilization, adsorption and movement with soil water) are frequently vital to the final outcome; such interactions are difficult to study in physical laboratory models. Additionally, physical models in the laboratory often bear little resemblance to field systems, thus the results of studies with packed soil columns, for example, may actually lead researchers to erroneous conclusions about pesticide mobility in the field. Controlled laboratory experiments with soil columns are still useful, but not for making field predictions (1). Laboratory columns allow one to study transport processes under controlled conditions, to identify cause and effect relationships and to test various conceptual transport models against experimental data. Extension of information gained from laboratory columns to field situations requires a careful assessment of the similarities and differences between the two systems. Mathematical models which are developed with field systems in mind, and tested first with laboratory column experiments, can be expected to be useful for field prediction if the appropriate equation parameters can be determined for the field system.

The possibility of modeling complex real-world problems involving pesticides has been enhanced markedly in the past 20 years by the availability of high-speed computers with capacity to solve large systems of equations numerically. A large number of simultaneous processes can be modeled as one integrated system. For example, the Agricultural Runoff Management (ARM) Model, completed by the U.S. Environmental Protection Agency in 1976, simulates runoff, snow accumulation and melt, sediment loss, pesticide-soil interactions, and soil nutrient transformations (2). The conceptual approach for the ARM Model was described by Bailey, et al. (3). This model is designed to assess principally the pesticide, nutrient and sediment losses in runoff from agricultural lands. Adsorption-desorption and leaching processes have an important role in determining the loss of pesticides in runoff, but apparently these processes were not modeled adequately for all of the pesticides with which the model was tested (4). The success of the model for some compounds and failure for others indicated the need for a better understanding of the mechanisms which control pesticide movement into the soil profile. Thus, while large, complex systems can now be modeled, there is a pressing need to be able to accurately model individual processes, which can then be incorporated as subprograms in a larger system. The difficulties of developing and validating models for even single mechanisms of contaminant transport in soils and groundwater systems have been emphasized in recent reviews (5,6).

In this paper I will limit the discussion to a consideration of hydrodynamic dispersion and adsorption as mechanisms which impact directly on the movement of pesticides into and through the soil profile. These two mechanisms are closely linked and thus need to be considered together. Volatilization and degradation, while equally important, are addressed in other papers in the symposium. The approach will be to consider first the general types of models which have been developed in the past 15 years, then, for both dispersion and adsorption mechanisms, examine (a) the nature of the mechanism, (b) some modeling approaches designed to simulate specific phenomena, and (c) alternative methodologies for determining key parameters. Brief attention will be given to other input requirements for useful field models.

The objectives of this paper are to describe the present status of modeling pesticide transport in soil water, to provide some historical perspective, and to indicate what might be considered research areas of highest priorty in our attempts to forecast pesticide mobility in the field. The paper is not a review of all relevant published research, but hopefully it reflects recent progress reported in English-language publications.

MATHEMATICAL MODELS OF CHEMICAL MOVEMENT IN SOIL WATER

There is a wide variety of models which have been developed to describe and/or predict solute movement in soils. The different basic approaches had their origin in areas of chemistry (chromatographic approaches), chemical engineering and hydrology. The series of key papers on miscible displacement of solutes in soils by Biggar and Nielsen in the early 1960's, summarized in (7), stimulated research on quantitative means of describing solute movement in soils, first with respect to salt and fertilizer movement and later with respect to pesticides and other toxic chemicals. A description of diffusion and convection-dispersion processes, accompanied by a summary of miscible displacement techniques and mathematical solutions of the dispersion equation, are given by Kirkham and Powers (8). Other helpful reviews describe a variety of solute transport models (9,10,11), and some reviews specifically address modeling the movement of pesticides (12,13,14).

In this section we will briefly discuss some of the equations that have been used in solute movement studies and indicate their advantages and disadvantages for use in prediction of pesticide movement. A rigorous treatment of this subject is provided by Leistra (14).

Simple Convection Model

If diffusion is neglected and a pesticide is transported in water by mass flow (convection) in "piston" fashion (without being dispersed in the direction of flow), the appropriate mathematical expression is

$$J = v\theta c \qquad [1]$$

where J is one-dimensional solute flux $[ML^{-2}T^{-1}]$, θ is volumetric water content $[L^3L^{-3}]$, v the average interstitial fluid velocity (Darcy flux divided by water content) with dimensions of LT^{-1} and c the solute concentration in the soil solution. (Use of θc allows solute concentration to be expressed in terms of the mass of solute per unit volume of soil rather than per unit volume of soil solution, and is necessary when solute transport equations are combined with water flow equations for transient water flow.) J represents the mass of solute passing through a unit area of soil per unit time. This simple expression has been used by a number of workers in empirical compartment-type models in which flowing soil water is imagined to pass from one compartment into another with a velocity of v along the axis of flow, and solute entering each compartment equilibrates instantaneously with solute already in the compartment before the next increment of flow. Some apparent dispersion is imposed by the way in which solute concentration in each cell is calculated by averaging incoming and remaining solute concentration in each compartment. The greater the compartment length ("theoretical plate height" in chromatography terminology), the more is the imposed apparent dispersion. The model has been used to successfully describe the distribution of inorganic salts in soil columns (15) and field soils (16) and effluent concentrations from columns (17). In other studies the movement of pesticides in soil columns was estimated by incorporating an independently measured adsorption coefficient in the equilibration calculation for each compartment (18,19,20). Swanson and Dutt (20) were the first to investigate the effect of non-singular adsorption-desorption relationships on pesticide movement through soil columns. Their compartment model accurately predicted atrazine concentrations in the effluent for two soils with different adsorption capacities.

While the results obtained with the simple convection-compartment model are surprisingly good in many cases, the arbitrary adjustment of compartment length in the model to achieve the calculated dispersion corresponding to that in the experimental data does not encourage widespread use of such models. I have discussed this approach for two reasons, in addition to the historical perspective provided: First, the simple convection equation is one of the building blocks of the convective-dispersive flow equation to be presented later, and essentially describes solute transport in the absence of diffusion and dispersion. A solute transport equation which adequately describes dispersion is essential for most applications; likewise an equation coefficient characterizing pesticide dispersion in field soils is a property of the flow system which we must be able to measure. If we cannot measure a meaningful dispersion coefficient for use in the more rigorous equation, the resulting prediction equation may prove to be almost as arbitrary as a compartment model based on Equation [1]. The second reason for discussing the simple equation is that models based on piston displacement appear to have some utility for approximating solute fronts in field soils under some conditions (21).

Dispersion Equation Neglecting Diffusion

An equation formulated on the basis of Fick's law of molecular diffusion, but with the coefficient D' $[L^2T^{-1}]$ being a dispersion coefficient rather than a diffusion coefficient, was proposed by Day (22),

$$\theta \partial c/\partial t = \theta D'(\partial^2 c/\partial x^2) \qquad [2]$$

in which x is distance [L] and t is time [T]; the other variables or constants were previously defined. This equation and others which follow are obtained by combining the appropriate flux equation with the equation of continuity, $\theta \partial c/\partial t = -\partial J/\partial x$. In the present case the flux is given by $J = -\theta D'(\partial c/\partial x)$. The derivation of [2] and its solution for a variety of initial and boundary conditions are presented elsewhere (8). Although Equation [2] has been found to satisfactorily describe the movement of inorganic solutes in field soils (23,24), the coefficient D' cannot be determined independent of the experiment, but must be obtained by fitting the solution of the equation to at least one set of experimental data (e.g. solute concentration versus depth for a given water flux over a given period of time). Also Nielsen and Biggar (25) have emphasized the limitations of a solute transport equation which does not incorporate fluid velocity effects on solute mixing in an explicit way. Thus it is evident that an equation which lumps too many processes into one parameter lacks the generality that is required for applications involving a variety of porous materials and flow velocities. This seemingly obvious conclusion is good to keep in mind when we are evaluating transport equations for their value in predicting pesticide movement in the field.

Diffusion-Dispersion Equation with Convection

The failure of Equations [1] and [2] to adequately describe solute movement in porous materials led investigators to develop the equation which is now most commonly used in modeling solute transport in soil water. The equation is derived by assuming that the one-dimensional solute flux through a unit soil area is the sum of fluxes due to three contributing mechanisms:

convection, diffusion and mechanical dispersion, the latter being due to the range of pore velocities which disperse the solute as it is moved by convection through the soil. The convection flux (J_1) is given by Equation [1] and the diffusion and dispersion fluxes can be expressed, respectively, as $J_2 = -D_e\,(\partial\theta c/\partial x)$ and $J_3 = -D_\ell\,(\partial\theta c/\partial x)$, where D_e is the effective diffusion coefficient for solute in porous soil $[L^2T^{-1}]$ and D_ℓ is the longitudinal dispersion coefficient $[L^2T^{-1}]$. Substitution of $J_1 + J_2 + J_3$ in the continuity equation and assuming for the present that both D_e and D_ℓ are independent of the distance x,

$$\partial\theta c/\partial t = -v\partial\theta c/\partial x + (D_e + D_\ell)\partial^2\theta\, c/\partial x^2 \qquad [3]$$

While some workers have studied the separate contributions of D_e and D_ℓ to the dispersion of solute (26), most have lumped them together so that $D = D_e + D_\ell$, with D being called the "apparent diffusion coefficient" (27), "spreading coefficient" (14) or simply "dispersion coefficient" (11). It is notable that researchers quickly recognized the difficulty of distinguishing the independent contributions of diffusion and longitudinal dispersion to the spreading of solute. Thus, even though the two distinct mechanisms were identified, the nearly impossible task of measuring their magnitudes in a flowing system required the use of a single coefficient, D, giving the much used convection-diffusion-dispersion equation

$$\partial\theta c/\partial t = D\partial^2\theta c/\partial x^2 - v\partial\theta c/\partial x \qquad [4]$$

I have chosen to leave θ inside the differential operators in each term to emphasize that soil water content is a variable in the dispersion equation when water flow is not steady, which is the more common case in field situations.

Some important facts about Equation [4] need to be understood lest it be applied indiscriminately with false expectations as to how well it will describe pesticide movement in soils. First, both v and D appear as constants in the equation, while in fact they represent mechanisms which frequently cannot accurately be represented by constants. The constant v in the convection term is calculated from the Darcy flux, q/θ, and thus represents an average velocity for the likely wide range of velocities expected in the broad spectrum of sizes of pores through which solution is moving. The wider the range of pore velocities, the less representative will an average velocity be. Wide deviations of velocities for individual pore sequences from the average velocity will cause solute mixing that is not described by the convection term, $v\,\partial c/\partial x$; this mixing must be described by the diffusion-dispersion term, $D\,\partial^2\theta c/\partial x^2$. Most experimental evidence suggests that D in [4] is a function of average velocity, with D increasing as velocity increases. Biggar and Nielsen (27) have reviewed this subject in some detail, providing evidence from laboratory column studies (28) and field studies (29,30) that an appropriate function may be $D = D_e + \lambda v^m$, in which λ and m are fitted constants and D_e is the effective diffusion coefficient (either assumed or measured) at a given soil water content. Smiles and Philip (31), on the other hand, have concluded from a laboratory study and theoretical considerations that D should be velocity-independent in unsaturated soils, except perhaps in coarse sands.

The diffusion coefficient D_e can be expected to increase as soil water content increases (27), but D_e is generally small relative to the composite coefficient, D, so that variations in D_e with water content may not be a problem. Laboratory studies have shown that D increases as water content decreases (30), but apparently this relationship has not been defined for field soils. In most field experiments the effects of pore velocity and water content on D would probably be confounded.

Despite the uncertainties noted above, the reasonable prediction of the distribution of non-adsorbed solute in a field soil with Equation [4] by Warrick et al. (29) is reason for cautious optimism. Variability of v and D in field soils (30) poses other problems which will be discussed later with regard to measurement of key parameters and model validation.

Convection-diffusion-dispersion equation with adsorption. The success of Equation [4] in describing the movement of non-interacting solutes in laboratory columns and in a few field studies has encouraged researchers to go one step further, and attempt to model the movement of solutes which interact with soil colloids; interaction with colloid surfaces can include cation and anion exchange, anion repulsion, or in the case of non-ionic organic chemicals (including most pesticides), adsorption-desorption. Incorporation of solute interaction into the model is accomplished by adding another term to the left-hand side of [4], giving

$$\partial\theta c/\partial t + \rho\partial S/\partial t = D\partial^2\theta c/\partial x^2 - v\partial\theta c/\partial x \qquad [5]$$

in which S is the adsorbed concentration, expressed in units of mass of solute adsorbed per unit mass of dry soil $[MM^{-1}]$, and ρ is the soil bulk density $[ML^{-3}]$. Note that ρS then has the same dimensions as θc, i.e. ML^{-3} or mass of solute per unit volume of soil. The adsorbed quantity is not a constant but is a function of the concentration in solution. The function may be quite simple, as in the case of instantaneous equilibrium adsorption with a singular adsorption-desorption relation, or the S-c function can be quite complex if a kinetic expression is needed. The use of S in Equation [5] requires that the appropriate adsorption function be defined. Several laboratory pesticide movement studies in the 1960's attempted to describe equilibrium adsorption with a linear function, such as $S = k_1c + k_2$, but this relation incorporated into the solution of Equation [5] often failed to adequately describe the early breakthrough of pesticide in the column effluent or the asymmetry ("tailing") in the concentration-effluent volume curve following emergence of the peak concentration in the effluent (10,11,14). Computed movement was generally poorest for the more highly adsorbed chemicals and at high flow velocities (14). Subsequently, researchers have explored a number of different approaches to account for adsorption effects, including both equilibrium and kinetic expressions. Summaries of several adsorption equations are presented by Boast (9) and van Genuchten and Cleary (10). Adsorption effects and their mathematical description will be discussed in more detail in a later section.

SOLUTE DISPERSION IN FIELD SOILS

At this point I want to focus on some challenging problems with which we are faced when we attempt to apply Equation [5] to predict pesticide mobility in field soils. This section will deal principally with (a) the solute dispersion process, (b) attempts to model the process, and (c) determination of parameters for solute transport equations. Adsorption enters into the discussion because the dispersion and adsorption processes are inextricably coupled, but adsorption aspects will be the subject of a subsequent section.

Structural Characteristics of Field Soils -- The By-Pass Problem

During the 1980 Annual Meeting of the American Society of Agronomy, a symposium with twelve papers addressed the subject "Water and Solute Flow through Soil with Large Pores." The existence of such a symposium indicates the increased interest in recent years in applying physical theory and mathematical modeling techniques to the solution of field problems involving water and solute transport. Some of the papers stressed the need for new approaches in applying transport theory to highly heterogenous, anisotropic soils. Some researchers question whether the Darcy equation and a solute transport equation such as Equation [5] are appropriate for many natural soils with extremes in pore sizes.

Also, I was interested to find in a recent issue of the Soil Science Society of America Journal (May-June, 1981) that both papers which occupy the Soil Physics section, deal with solute movement in soils, but the research approach and outlook of the two are quite different. The first (32) states the following in the Abstract: "The analysis (of hydrodynamic dispersion with velocity independent dispersion coefficient) is demonstrated using a chemically inert sandy soil. The results show that during transient, unsaturated flow, a simple piston-flow model described the process over a range of water contents. The method may be extended to explore dispersion in structured and chemically reactive soils." The second paper (33) states in the discussion: "In soils which exhibit strong structure, water and salt flow down the larger pores, channels, cracks, root holes, worm holes, and ped faces can be significant. Soils without these structural features, such as uniform fine sandy loam and carefully packed laboratory columns, exhibit more uniform displacement. Thus, laboratory studies carried out with no appreciable soil structure may not be applicable to soils with distinct structure." Both works reported research results which likely led to valid conclusions for the particular soil-water-solute system studied in each case. But care must be exercised in applying techniques or conclusions developed in one system to another system which may differ significantly in pore-size distribution or another critical property.

The fact that equations developed from rational physical principles do work in some cases and do not work in other cases should lead us to evaluate the profile characteristics of specific soils with regard to physical and chemical properties that impact on water and solute movement. This has been done in some studies with soils evidencing heterogeneity and/or anisotropy in their hydraulic properties, particularly the hydraulic conductivity-water content relationship.

In studies of water movement through Houston Black clay, a Udic Pellustert which undergoes shrinkage and swelling with drying and wetting cycles, Ritchie et al. (34) demonstrated that most of the water contained within soil peds (structural units) was not active in the flow process in comparison to water in larger pores around the peds, especially when the soil was nearly water saturated. Measurements of nitrate and chloride movement in the same soil (35) indicated that applied chemicals were transported in percolating water through large connected pores, by-passing the water inside the soil peds.

We had measured a similar phenomenon in a non-swelling, highly structured Torrox soil (36). The field site had been tilled to a depth of about 0.4 m (common for sugarcane in Hawaii), and was underlain by a moderately permeable subsoil with coarse, prismatic structure. The potassium salt of picloram herbicide (a weak organic acid) was applied in a small volume of water to the previously wetted soil prior to ponded irrigation with 0.24 m water. Picloram concentrations in the soil solution one week after irrigation were obtained at various depths below the soil surface with porous ceramic suction probes; the results are shown in the left-hand graph in Figure 1. Picloram had moved below 0.80 m and was even detected by a deep probe at 1.43 m. Two subsequent weekly irrigations of 0.12 m water each resulted in the profile concentration curves in the middle and on the right of Figure 1. The deep penetration of some picloram with the first irrigation and retention of the picloram "peak" at about 0.15 m after application of a total of 0.48 m water led to the conclusion that rapid, non-uniform water flow was occurring during irrigation and early drainage. Piston displacement of the picloram (assuming the laboratory-measured linear adsorption coefficient of 2×10^{-4} m^3/kg) would likely have moved the peak to a depth of about 1.0 m, based on an average water retention of 0.40 m^3m^{-3} in the profile. A companion study of nitrate movement (37) indicated a similar by-passing of solute within soil peds, although nitrate moved more readily and uniformly than did picloram, probably because nitrate was not adsorbed. A comparison of nitrate movement when irrigation was applied immediately or one week after nitrate application to the soil revealed that initial equilibration rendered the nitrate less mobile, presumably because of diffusion of added nitrate into micropores within peds.

While our proposed mechanisms for early solute breakthrough and subsequent slow movement of the picloram peak in the Torrox soil were somewhat speculative at the time, later soil column studies on the Molokai soil (38,39) confirmed the importance of bi-modal pore-size distributions to picloram transport. Comparisons with other soils revealed that secondary peaks appeared in the effluent breakthrough curves of Molokai soil aggregates but not in the curves for soils which were less aggregated. These results were explained by the very high hydraulic conductivity associated with

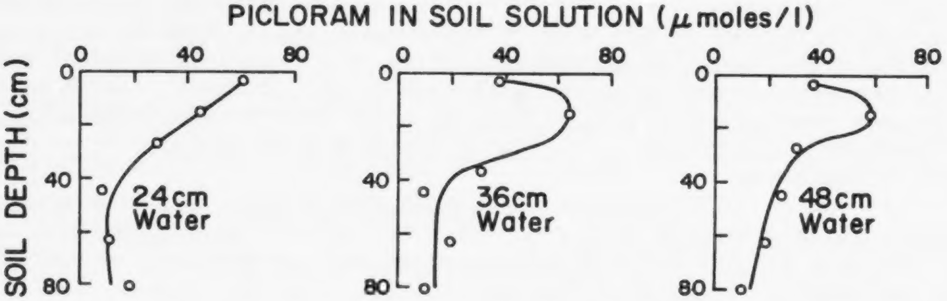

Figure 1. Picloram distribution in the profile of Molokai soil (Typic Torrox) after successive ponded applications of water at weekly intervals; chemical applied at 20 kg acid equivalent per hectare. From Rao et al. (36).

macropores in the Molokai soils (38) and by the relative size of internal and external pores observed in scanning electron micrographs of aggregates (39).

In recent years, abundant evidence has been provided for by-pass flow through large pores or cracks in the soil (e.g. 40,41,42). Extensive flow channeling in macropores was indicated by rapid deep penetration of chloride from limited sprinkler irrigation using water containing a chloride tracer (40). One soil had been planted to bluegrass for 5 years, but a tilled soil showed similar behavior. Calculated displacement of pore water initially in the soil near the surface generally ranged between 7 and 30% of the original water for water applications of about 0.015 to 0.04 m (41). The limited displacement of water initially in soil aggregates indicated the lack of uniform flow and the likelihood that by-pass flow was a common occurence on these soils. Thomas and Phillips (42) suggest that many "hydrologists, soil physicists, and soil scientists in general" do not recognize the importance and widespread occurrence of macropore water movement; they cite numerous published observations (from as early as 1882) to emphasize that the phenomenon has been recognized by numerous workers but is considered by many to be characteristic of a few unique soils.

Certainly the process of dispersion in soils has been understood for a long time. Gardner and Brooks (43) in presenting evidence for the dispersion induced by variable velocities in different sized pores stated: "Large pores or combinations of large pores give rise to a certain amount of channeling". It may be significant that these workers studied salt movement in both laboratory packed columns and field plots, thus observing the generally higher dispersion in field soils. Biggar and Nielsen (44), in their carefully designed and conducted laboratory experiments, demonstrated the striking effects of both aggregate size and fluid velocity on dispersion as evidenced by the shapes and positions of effluent breakthrough curves. Emphasizing the effects of velocity distribution on dispersion, they reasoned as follows: "Because the total number of contacts between aggregates in the column decreases with increasing aggregate size, the proportion of the total flux through the pores in the aggregates will decrease with increasing aggregate size. Thus, as the aggregate size increases, mixing in the column becomes less complete and the effluent concentration is dominated by flow through the large pores. In effect this means that tracer will appear in the effluent earlier and a greater throughput volume will be required to reach $c/c_0 = 1.0$ the larger the aggregate size." This description of dispersion in packed columns of soil aggregates appears to explain the major processes involved in the movement of picloram and nitrate through Molokai soil in the field, as I discussed previously in reference to Figure 1. Thus, laboratory studies under controlled conditions allow us to study the nature of the processes involved; only the magnitude of the effects differ between laboratory and field systems. But striking differences in poresize distributions and continuity of pores can result in very different solute transport in the same soil material, as shown in a comparison of packed columns of aggreates, soil cores, and field plots (45).

The research of Bouma and Anderson (46,47,48) is especially notable because of the way in which they related the morphological characteristics of structured field soils to water and solute movement. In measurements of chloride movement through columns of structured soil (47,48) they found that two soils having the same soil texture had very different solute transport characteristics. Both soils were Hapludalfs with silt loam texture, but one had coarse prismatic structure and the other had medium subangular blocky structure. Dispersion coefficients, obtained by fitting the solution for Equation [5] to effluent concentration data, were $D = 4.6 \times 10^{-9}$ to 1.2×10^{-8} m^2s^{-1}(0.4 to 10 cm^2 day^{-1}) for saturated soil columns with prismatic structure and about $D = 3.0 \times 10^{-7}m^2s^{-1}$(260 cm^2 day^{-1}) for the subangular blocky structure. Solute breakthrough curves for unsaturated columns generally evidenced more by-passing of soil pores than did saturated columns particularly in the soil with blocky structure (48). In some cases, the theoretical equation could not be fitted to the breakthrough data, so values of D could not be obtained.

In summary, there is conclusive evidence that in structured field soils, which are much more common than either single grained or massive soils, water in micropores within peds is often by-passed by water flowing through large void spaces. The pattern of water movement in such soils, whether the soil is saturated or unsaturated, results in extreme dispersion of solutes moving with the water. If some of the soil water is actually isolated from the water in conducting pores so that there is no continuity of water by way of connecting pores or water films, then Equation [5] is not valid, unless it can be appropriately modified (49). Some attempts at modifying the dispersion equation are presented in the next section. There appears to have been far too little effort to characterize the geometry of pore sequences in structured soils. Such efforts might be rewarded with a much better understanding of water and solute movement in field soils and improved possibilities of predicting the movement of pesticides and other solutes.

Attempts to Model the Dispersion Process in Structured Soils

In view of the apparent importance of micropore water which is excluded from active flow in many field soils, I will focus principally on recently developed models which consider mobile and immobile water in relation to solute dispersion.

A number of models based on Equation [5] were developed in the 1970's in attempts to account for adsorption effects on pesticide movement in soils. Van Genuchten and Cleary (10) give an excellent review of these developments, to which J.M. Davidson and his associates and M.Th. van Genuchten and his associates contributed substantially. The models differed primarily in the way in which S in the term $\partial S/\partial t$ in [5] was formulated to handle several possible types of adsorption behavior:

(a) adsorption equilibrium with linear or non-linear but singular adsorption isotherms;
(b) equilibrium adsorption but with non-singular, non-linear isotherms;
(c) kinetic non-equilibrium with linear or non-linear adsorption.

The extent to which each of the adsorption models succeeded depended on the particular soil and chemical involved and on flow velocity. None of the resulting flow models accounted for mobile and immoile water, until a precursor of the model to be discussed here was developed by van Genuchten, Davidson and Wierenga (50). A comparison of (a) their FREQ model (Fraction of soil in Equilibrium with mobile water) with (b) Equation [5] incorporating various adsorption submodels representing S, indicated that physical non-equilibrium (due to water in micropores being excluded from the mobile phase) accounted for non-symmetrical effluent concentration curves as well or better than some of the previous adsorption approaches.

The next step in this development was to modify the model of Coats and Smith (51) to accommodate adsorption of pesticides in both mobile and non-mobile phases (10,52). The model envisions five regions in the soil:

1. Air space
2. Mobile water, in inter-aggregate pores, which transports solutes by convection with dispersion.
3. Immobile water inside aggregates and at the contact points of aggregates and particles
4. A dynamic soil region in adsorption equilibrium with the mobile water phase
5. A stagnant soil region in which adsorption-desorption is limited by diffusion from the mobile water phase through the immobile water phase.

A parameter f is defined as the fraction of the sorption sites which is in direct contact with mobile water; thus f determines the relative proportions of the soil volume which are characterized either dynamic or stagnant. When f = 0 all adsorption occurs in the stagnant region. The resulting transport equation, an extension of Equation [5], in its most general form is

$$\partial(\theta_m c_m)/\partial t + \partial(\theta_{im} c_{im})/\partial t + \partial(f\rho S_m)/\partial t + \partial[(1-f)\rho S_{im}]/\partial t$$
$$= \partial(\theta_m D \partial c_m/\partial z)/\partial z - \partial(\theta_m v_m c_m)/\partial z \qquad [6]$$

in which the subscripts m and im refer to mobile and imobile regions, respectively and $v_m = q/\theta_m$, q being the Darcy flux.

To describe diffusion between the mobile and immobile regions, van Genuchten and Wierenga (52) added a sorptive component to the diffusion equation of Coats and Smith (51), giving

$$\partial\theta_{im} c_{im}/\partial t + (1-f)\rho\partial S_{im}/\partial t = \alpha(c_m - c_{im}) \qquad [7]$$

in which α is a mass transfer coefficient, which has subsequently been shown to be dependent on other system parameters(53). Equations [6] and [7] describe the movement of an adsorbed pesticide through structured soil when θ_{im}, θ_m, f, v , α, ρ, S_m and S_{im} are specified. When equilibrium, Freundlich-type adsorption is assumed, the number of dependent variables can be decreased from four to two, and with some simplifying assumptions, the mathematical solutions are expressed in terms of four independent parameters. Only the retardation factor ($R = 1 + \rho K/\theta$, in which K is the linear adsorption coefficient) can be independently determined; the others must be assessed by curve fitting procedures (10,11). Equations [6] and [7], with appropriate simplifications for constant water flux, successfully predicted 2,4,5-T movement through water saturated packed columns of clay loam aggregates less than 0.006 m in diameter. In this system only 50% of the soil water was calculated to be mobile, this result being obtained by applying the transport equations to the movement of tritium tracer. The parameter f for the 2,4,5-T experiment was 0.40, indicating that 40% of the adsorption sites were located in the dynamic regions associated with rapidly moving water in macropores and 60% of adsorption sites were in the micropores.

I have discussed the model of van Genuchten and Wierenga in some detail because it represents a recent development in deterministic, process oriented models which specifically addresses the problem of mobile and immobile water associated with structured soils. It appears to have promise for prediction of pesticide movement. The principal limitation of the approach presented above is that most of the key parameters in the equations must be obtained by least-squares fitting of the appropriate mathematical solutions to effluent concentration data. The curve fitting techniques are available (11), but there is considerable uncertainty as to whether a good fit of the conceptual model to experimental data actually constitutes confirmation of the designated processes inherent in the model (54,55). The need for methods to determine key parameters independent of actual measurement of pesticide movement is apparent. Ultimately we are interested in "forecasting" pesticide mobility in practical field situations; this will require the development of methods to measure or estimate relevant parameters. Recently, Rao et al. (56) demonstrated that independently measured parameters for a synthetic media with spherical porous "aggregates" gave good predictions of solute movement in columns with equations similar to [6] and [7]. Whether or not independent measurement of parameters for field soils is possible remains to be seen. The more detailed is the specification of physical and chemical mechanisms controlling pesticide transport, the greater will be the task of determining the parameters. Extremely simple models, such as that proposed by Addiscott (57), require much less input than the model defined by Equations [6] and [7], but such simple models must essentially be calibrated for a given soil and water flow regime, and thus lack the generality that is desirable in a predictive model.

Determination of Dispersion Coefficients for Field Soils

Although the measurement of key parameters required in solute transport equations has been considered briefly above, a few more comments on the determination of dispersion coefficients in field soils is appropriate.

Dispersion coefficients for packed soil columns are usually determined for the flow conditions of interest by a least-squares fit of the appropriate mathematical solution to effluent concentration data for a non-interacting solute. This same approach was used by Anderson and Bouma (47,48) for columns of structured soil. In some cases, especially when solute was transported in water infiltrating under ponded conditions into previously drained columns, D values could not be calculated; the equation for convective-dispersive-diffusive transport, Equation [4] in this paper, apparently did not describe the rapid breakthrough caused by flow by-passing. When a synthetic porous crust was established at the surface of soil columns so that unsaturated flow conditions were achieved, the chloride breakthrough curves were shifted to the right but still did not have shapes that could be described by the dispersion equation. The early breakthrough indicated significant by-pass flow even with unsaturation.

The crust technique of Anderson and Bouma (48) was adapted by Khan and Green (58) to measure the in situ value of D in Equation [4] for a highly structured Torrox soil located near the site on which the data in Figure 1 were obtained. A steady solution flux of 8.64×10^{-6} ms^{-1} (10 cm day^{-1}) was established in an in situ soil column 0.30 m in diameter by 0.80 m long. Nitrate concentrations obtained from extracts of soil samples taken at depth intervals of 0.05 m were used to determine D from an appropriate solution to the dispersion equation. Equation [4] described the data well, and the procedure yielded D values of 1.5×10^{-7} and $2.5 \times 10^{-7} m^2s^{-1}$ for two sites a few meters apart. Measurement of D on unsaturated soil ($\theta = 0.39 m^3m^{-3}$) probably minimized rapid flow through macropores so that Equation [4] was applicable. The dispersion coefficients were required in a simulation study of nitrogen transport and transformation when nitrogen fertilizer is applied in irrigation water (59). Although D is likely a function of θ and v in [4], the limited range of θ and v under high frequency, low intensity irrigation seemed consistent with the use of a constant D. The crust technique allows the determination of dispersion coefficients in field soils for various water content-flux combinations by varying the permeability of the crust.

Another technique of measuring D in unsaturated field soil was used by van de Pol et al. (60). Steady water flow was maintained by applying water at a constant flux of $1.7 \times 10^{-5} ms^{-1}$ (2 cm day^{-1}) with a drip irrigation system having an emitter in every square of a 0.3m x 0.3m grid system on an 8 x 8 m field plot. Chloride and tritium were used as tracers. Seven porous ceramic cups at various depths down to about 1.2 m allowed sampling of soil solution, which was analyzed to obtain tracer concentration versus time at various depths; values of D were then calculated for each depth. The geometric mean value of D from all probes for this non-uniform profile (clay over silty clay over silty loam over sand) was $3.2 \times 10^{-6} m^2s^{-1}$.

When one wants to measure the dispersion coefficient appropriate for the water-saturated condition the experiment appears easier to conduct because water can merely be ponded at the surface and solution sampled with suction probes (30). However, in soils with large pores that contribute to by-passing of water within peds, solution concentrations obtained with a suction probe under saturated conditions may not be representative of soil in that horizontal plane (10,36); in addition the solute concentration curves measured under such conditions would likely give a poor fit to the solution of the flow equation.

Whether or not suction probes are an appropriate sampling tool in heterogeneous soil (with respect to hydraulic conductivity) may be principally a matter of scale. Fried (61) addressed this subject in reference to dispersion in groundwater aquifers and concluded that "it is compulsory to make in-situ experiments to collect longitudinal dispersion coefficients, as laboratory results completely differ from field values." In general, conventional soil cores and suction probes do not adequately sample a representative elementary volume (REV) with respect to hydraulic conductivity and solute dispersion, particularly in soils with large void spaces and at high water contents. Beven and Germann (62) suggested that in order to obtain a meaningful spatial average, a suitable REV for a combined micropore/macropore system might be 1 to 10 m^2 in area with a depth corresponding to the distribution of macropores in the soil profile. Much more could be said about sampling, but that subject is beyond the scope of this paper. However, sample or plot size and the number of samples required are not only matters of concern to the statistician, but may be critical for the researcher attempting to characterize dispersion in a heterogenous soil.

PESTICIDE ADSORPTION IN RELATION TO MOBILITY

During the 10-year period between about 1965 and 1975 there was a massive, non-orchestrated research effort in the United States directed toward gaining a better understanding of pesticide behavior in the environment. With broad public support the federal government provided unprecedented financial backing for pesticide research through federal agencies concerned principally with agriculture, the environment in general, and water in particular. The availability of funds motivated many soil chemists, soil microbiologists, and soil physicists to investigate aspects of pesticide behavior related to their professional skills and interests. Pesticide adsorption on soils is one area of research that received the attention of a host of soil chemists and other scientists for several years. Many continue to contribute new ideas and approaches to pesticide adsorption research, but funding for this subject has diminished and research activity is modest compared to former days. This background perspective is relevant to our present discussion in that (a) a huge body of information on pesticide adsorption in soils and sediments has been accumulated in the past 15 years, (b) there is a need to re-examine the basic information that was developed during this period of fruitful research and apply the relevant principles to our understanding of new chemicals, and (c) the likely low level of funding available for pesticide adsorption research in the future makes it imperative that researchers indentify the knowledge gaps that most hinder our understanding of pesticide behavior in soil-water systems and invest their efforts where they will count the most.

Numerous comprehensive reviews of pesticide adsorption research are available, although most were published six to ten years ago (63,64,65,66,67, 68). In general the information summarized in these reviews is currently useful even though some of the compounds studied are no longer in common use. Two recent reviews focus on specific information requirements: Calvet (69) identifies aspects of herbicide adsorption that are particularly useful in understanding herbicide mobility and uptake by plants and suggests areas which most need additional research effort. Rao and Davidson (70) have summarized existing information on pesticide adsorption that has particular relevance to prediction of pesticide movement to non-target areas. They provided a critical evaluation of various adsorption methods and compiled a data base of adsorption distribution coefficients for a large number of pesticides. In view of these contributions, I will limit the present discussion to only those aspects of pesticide adsorption from solution that seem particularly relevant to our subject, forecasting pesticide mobility in soils, and especially in relation to the previous section in which the interaction of dispersion and adsorption was considered.

Adsorption Process and Its Description

Adsorption of a pesticide from solution onto the soil colloids reduces the concentration in solution. If the soil solution is moving down through the profile under the gravitational potential, a reduction in the concentration of pesticide in solution effects a reduction in the downward flux of pesticide, as indicated by the flux equation which led to Equation [4], i.e.

$$J = v\theta c - D\partial\theta c/\partial x \qquad [8]$$

Thus if adsorption reduces the concentration, c, to c = 0, the flux will be zero also. And if the downward liquid flow velocity, v, is zero the downward flux of pesticide is limited to that associated with diffusion, so that pesticide movement is negligible. This simple analysis may appear trivial, but it summarizes the impact of adsorption on pesticide movement through the soil profile. The two principal physical phenomena controlling the movement of non-volatile pesticides in the soil are adsorption and water flux. Thus, while the dispersion phenomenon which we discussed in the last section is especially important to the distribution of non-adsorbed or slightly adsorbed pesticides, adsorption is probably the dominant mechanism controlling the movement of most pesticides.

Equilibrium adsorption. Adsorption reactions proceed quite fast in relation to the time frame normally appropriate to pesticide behavior in field soils. Rao and Jessup (5) indicate that generally 60 to 80% of the reaction is completed within a few minutes and equilibrium is achieved within a few hours in batch suspension adsorption measurements. The rapid approach toward equilibrium may justify the use of equilibrium adsorption data to describe the relationship between concentration of pesticide adsorbed on soil and the concentration in solution for most soil-water regimes (55). This relationship is conveniently represented graphically by an "adsorption isotherm", i.e. a plot of concentration adsorbed (mass of pesticide per unit mass of dry soil) against the corresponding equilibrium concentration in the solution (mass of pesticide per unit volume of solution); because adsorption is usually temperature dependent each curve should represent adsorption at a given temperature, hence the use of the term "isotherm". The concentration dependence of adsorption varies widely between pesticides on the same adsorbent and between adsorbents with the same pesticide. The shape of the isotherm varies widely also, so that no one mathematical expression can provide a universal adsorption equation for use in pesticide transport models. A number of the equilibrium adsorption equations which have been proposed are presented elsewhere (5,9,10). Among these, the two which have gained the widest acceptance for use in transport models (5) are the linear model,

$$S = S_o + K_d c \qquad [9]$$

and the Freundlich model,

$$S = K_f c^N \qquad [10]$$

S and c have the same definitions and dimensions as in Equation [5] of the first section, and K_d, S_o, K_f and N are empirical constants, with S_o usually being assigned the value of zero. The value of N in the Freundlich power function is usually less than one, so that the resulting isotherm is concave downward, that is, the adsorbed quantity increases rapidly as concentration is increased at low concentrations, but adsorption changes at high concentrations in solution are much less. However, in some cases N exceeds one. Compilations of the coefficients for many compounds (65,70) suggest that values of the coefficient N in Equation [10] commonly range between 0.75 and 0.95. It has been suggested (70) that for many modeling purposes a linear isotherm can be used in lieu of the Freundlich isotherm with acceptable error. The error introduced by this approximation depends on the value of N and the solution concentration, as shown in Table 1 from calculations given by Hamaker and Thompson (65). When N = 1 in [10] the two equations are equivalent (for $S_o = 0$ in [9]), as shown by the ratio of 1 in the top row in the main body of the table. As the value of N decreases, the linear approximation becomes less and less satisfactory, especially at high and low concentrations. A graphical presentation of the error versus solution concentration has also been presented (70). Although $N \leq 1$ is the most common situation, the exceptions need to be recognized. In a study of atrazine adsorption on soil from three horizons (71), we found that adsorption on the subsoil was negligible at low solution concentrations and difficult to measure reproducibly by the batch equilibrium method (72). With increased concentration, however, adsorption increased in such a way that the isotherm had a concave upward shape. The seemingly negligible adsorption at low concentrations may be more important to pesticide resistance to leaching than a small value of the distribution coefficient would suggest, especially if diffusion is the rate controlling process in removal of adsorbed pesticide from the micropores of aggregates. This mechanism was suggested (36) as the probable reason for the unexpected retardation of picloram movement shown in Figure 1.

Since even a fairly complicated transport model, such as that represented by Equations [6] and [7] combined with appropriate initial and boundary conditions, can accommodate adsorption functions such as Equation [10] when numerical solutions are used (73), it may not be necessary to represent a curvilinear adsorption isotherm by a linear approximation. The Freundlich equation is probably satisfactory for most pesticide-soil combinations.

An additional adsorption complication with regard to pesticide transport modeling is the frequently measured "non-singularity" in the adsorption-desorption process. For systems which evidence this behavior the desorption curve lies above the adsorption curve, such that the value of N in Equation [10] for desorption (N_d) often has a value around two times the value of N for adsorption (N_a), i.e. $N_d/N_a \approx 2$. This lack of singularity has been commonly referred to as "hysteresis", in reference to the analogous behavior of gas adsorption in porous media. However, in contrast to gas adsorption, there is no thermodynamic rationale for the lack of reversibility in adsorption of non-ionic organic chemicals from aqueous solution. The phenomenon has been measured for many soil-pesticide combinations, and has been confirmed by careful experimentation in some cases (e.g. 74). In some other cases, however, the apparent non-singularity appears to be an artifact of the procedure normally used to measure adsorption-desorption curves by

Table 1. Ratio of Adsorbed Quantities Calculated by the Freundlich and Linear Equations at Different Concentrations of Pesticide in Solution.

RATIO: $\dfrac{S = K_f c^N}{S = K_d c}$

N	Solution concentration, c (μg/ml) 0.01	0.1	1	10	100
1.0	1	1	1	1	1
0.9	1.6	1.3	1	0.79	0.63
0.8	2.5	1.6	1	0.63	0.40
0.7	4.0	2.0	1	0.50	0.25
0.6	6.3	2.5	1	0.40	0.16
0.5	10.0	3.2	1	0.32	0.10

Summarized from Hamaker and Thompson (65).

batch equilibration (70). Rao and Davidson (70) describe two alternative equilibration methods which avoid the usual repeated dispersal-equilibration-centrifugation cycles. Some pesticide-soil combinations did not evidence the non-singular adsorption behavior when the alternative procedures were used. More research is obviously needed on methods of determining adsorption-desorption of pesticides from solution.

Non-equilibrium adsorption. Despite the fact that adsorption measurements in a slurry system indicate a rapid approach to equilibrium in most cases, the assumption of instantaneous adsorption is likely invalid for field soils when the water flux is high, and especially so with structured soils in which there is a tendency for flow by-passing. Attempts to use kinetic adsorption models to describe pesticide transport at high water fluxes have not been successful (50).

In addition to the short-term kinetic effects, there is also evidence that in some pesticide-soil systems adsorption continues to increase at a very low rate after an apparent equilibrium has been reached. This subject was discussed in some detail by Hamaker and Thompson (65), who concluded: "There is an urgent need for serious investigation of this aspect of soil adsorption because of its practical importance". To my knowledge there has been little if any further definitive research on long-term adsorption changes since 1972 when Hamaker and Thompson's review was published. Their conclusions were based partly on the results of Obien (75) who calculated the ratio of atrazine adsorbed to atrazine in solution (approximating K_d) for a slurry system over a period of 60 days. Chemical hydrolysis of atrazine to hydroxyatrazine over the course of the study required that the quantity of atrazine adsorbed and in solution at a given time be determined by extraction with methanol and separation of atrazine and hydroxyatrazine. The approach was simple yet quite unique; the experimental procedure is diagrammed in Figure 2. During the 60-day period as the amount of atrazine in the system decreased due to hydrolysis, the adsorbed fraction of the remaining atrazine in the system actually increased, so that the calculated apparent K_d increased with time. The results for one of the four soils studied are shown in Figure 3, which is drawn from tabular values (75). Corresponding K_d values were 0.0017 $m^3 kg^{-1}$ (1.7 ml/g) after a conventional 4-hour batch equilibration and 0.0034 $m^3\ kg^{-1}$ (3.4 ml/g) at 60 days. Such an increase in atrazine adsorption over time, if occurring in field soils, would definitely have an impact on atrazine mobility.

Another study with which I was associated a few years ago provided some pertinent information on the desorption of "aged" diuron herbicide in soil. As part of his analysis of non-singularity in the adsorption-desorption of diuron on some Hawaii soils, Mukhtar (74) briefly examined the desorption of diuron from a Humoxic Tropohumult soil (3.2% organic matter) which had received an application of diuron herbicide 18 months earlier; the field is located in an area receiving 1.8 to 2.3 m annual rainfall and was planted to sugarcane. When a field soil sample was equilibrated with water the quantity of residual diuron adsorbed in relation to the quantity in solution was in line with the desorption isotherm for freshly applied diuron, but was above that for the adsorption isotherm. These results suggested no "aging" effect, but only a non-singularity for the adsorption-desorption process.

The mechanisms which have been proposed for non-singular adsorption (65, 70) are likely responsible also for the apparent increase in adsorption with aging. The effect of these phenomena on pesticide mobility is to retard movement more than would be anticipated from conventional adsorption measurements; this is good from the standpoint of water pollution. Thus unless "by-pass water flow" is moving pesticides to greater depths than expected because of non-equilibrium adsorption soon after pesticide application, actual movement toward groundwater would probably be more conservative than calculations would indicate.

Another matter should be mentioned with regard to pesticide retention by adsorption. When the applied pesticide undergoes progressive degradation, each degradation product will have its own adsorption-desorption characteristics, and thus will move with water independent of the parent compound, perhaps faster, perhaps slower. It is quite unusual to find adsorption-desorption isotherms for degradation products in research reports which have details on the adsorption and degradation of the parent compound.

Hamaker and Thompson (65) in concluding their thorough analysis of pesticide adsorption in soils gave the following perspective:

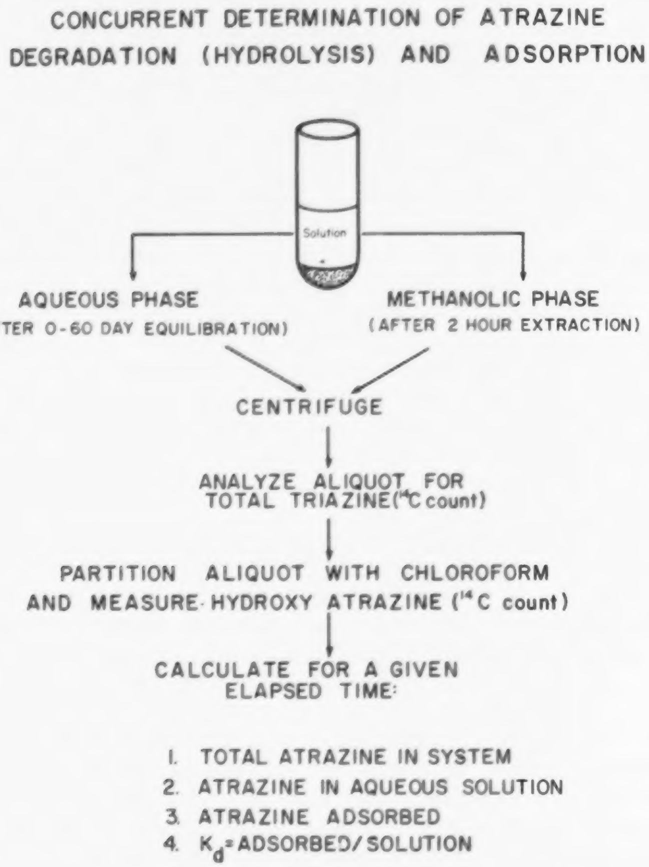
CONCURRENT DETERMINATION OF ATRAZINE
DEGRADATION (HYDROLYSIS) AND ADSORPTION
Solution
AQUEOUS PHASE
(AFTER 0-60 DAY EQUILIBRATION)
METHANOLIC PHASE
(AFTER 2 HOUR EXTRACTION)
CENTRIFUGE
ANALYZE ALIQUOT FOR TOTAL TRIAZINE (^{14}C count)
PARTITION ALIQUOT WITH CHLOROFORM AND MEASURE HYDROXY ATRAZINE (^{14}C count)
CALCULATE FOR A GIVEN ELAPSED TIME:
1. TOTAL ATRAZINE IN SYSTEM
2. ATRAZINE IN AQUEOUS SOLUTION
3. ATRAZINE ADSORBED
4. K_d = ADSORBED/SOLUTION

Figure 2. Diagram of procedure used to measure changes in atrazine adsorption on soil in a 60-day period. From Obien (75).

"As we attempt to look down the corridors of the future with respect to research in this area, we see two chief directions of opportunity and need: (a) achieving a better fundamental understanding of the nature of the soil adsorptive surface and (b) developing valid kinetics for adsorption by soil. These two areas, in particular, are needed for the application of sorption to the practical problems that attend the use of chemicals in soil." They continued: "Upon these two advances in fundamental understanding, we can expect an increased ability to handle a number of applications of adsorption knowledge; and perhaps the most important of these is leaching. At the present time, the correlation between leaching and sorption is inadequate, largely because there is no distinction between short-term and long-term adsorption. Therefore, we can predict only the leaching that would occur on freshly applied material, and it is not within our knowledge at present to deal with material that has been in the soil for some time, for which the leaching process is much less effective." These conclusions, expressed about 10 years ago, are equally valid in 1981, and especially so from the standpoint of "forecasting pesticide mobility in soils". Perhaps the prediction of short-term behavior of pesticides in soils is in itself such a difficult task that we have not been prepared to explore even more complex problems. The challenge remains to assess the adsorption-desorption relationship for pesticides and their principal degradation products over extended periods of time.

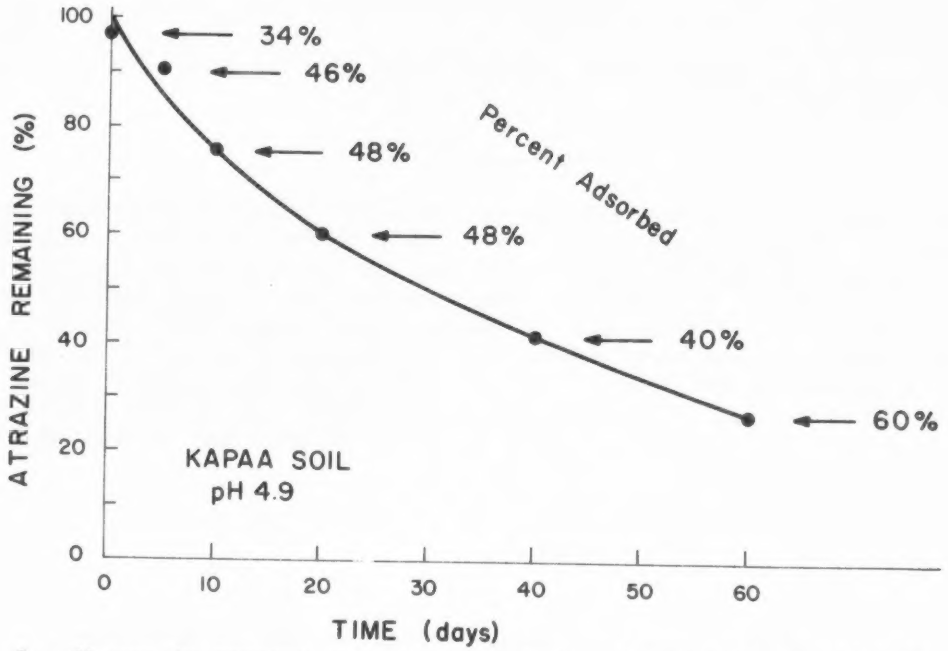

Figure 3. Change in percent atrazine adsorbed on Kapaa soil (Typic Gibbsiorthox) during a 60-day period in which the total amount of atrazine decreased by hydrolysis. From Obien (75).

Modeling Adsorption for Use in the Dispersion Equation

The various equations which have been proposed to describe both equilibrium and kinetic adsorption have been summarized elsewhere (9, 10). The two most frequently used equations for equilibrium adsorption are the linear function and the power (Freundlich) function, expressed by Equations [9] and [10]. The linear equation has the distinct advantage of simplifying the solution of Equation [5] in that an analytical solution is available (10). Numerical techniques provide solutions when [10] is used to describe adsorption. In general, numerical solutions will likely be required for most practical situations because adsorption of most pesticides on soils is highly correlated with soil organic matter content, which generally decreases with depth; thus different adsorption parameters may be required for various layers in the soil profile. Selim et al. (76) have studied the layered-soil problem with laboratory columns and predicted effluent concentrations in this system with Equation [5].

Two kinetic adsorption equations were evaluated by van Genuchten et al. (50) in a laboratory study by predicting column effluent concentrations with [5] using the kinetic equations to describe $\partial S/\partial t$. The more complicated of the two equations, derived by Lindstrom et al. (77), gave about the same results as Equation [11]

$$\partial S/\partial t = k_2(\theta k_1 c^N/\rho k_2 - S) \qquad [11]$$

Equation [11] is a first-order kinetic rate equation, with first-order forward, k_1, and first-order backward, k_2, kinetic rate coefficients (T^{-1}). At equilibrium ($\partial S/\partial t = 0$) Equation [11] reduces to Equation [10]. Other investigators have simply differentiated Equation [10] with respect to time to get Equation [12],

$$\partial S/\partial t = K_f N c^{N-1}(\partial c/\partial t) \qquad [12]$$

but this equation does not incorporate different rates for adsorption and desorption. Although both of the rate equations tested against column data for picloram displacement gave good results at low flow velocities, neither equation was satisfactory at high flow velocity (50). These negative results led van Genuchten and associates to explore other approaches, resulting in the development of the model represented by Equations [6] and [7]; the latter approach emphasizes the rate of diffusion of solute into immobile water rather than the rates of adsorption and desorption. It is likely that the mass transfer coefficient, α, in [7] actually includes the adsorption kinetic effects.

Determination of Adsorption Parameters

Equilibrium adsorption at various concentrations of pesticide in solution can be determined either in a batch-suspension system or in a flow system. An assessment of a number of the alternative procedures that have been proposed was presented by Green et al. (78). The relative merit of each of the methods depends on the objectives of a study. In general, the batch method can be expected to give slightly higher amounts of adsorption at a given solution concentration than a flow method which protects soil aggregates from dispersion. However, in some pesticide-soil combinations the two methods give essentially the same results (79). The batch method was found to be inadequate for low-level pesticide adsorption, such as in soils with low organic matter, because of the indirect determination of adsorption (72), while direct extraction and measurement of adsorbed pesticide after establishing equilibrium gave good precision even with very low adsorption (79).

Determination of kinetic adsorption coefficients that will have meaning for field soils is a difficult task that has not been studied much, to my knowledge. The flow procedure developed by Cheung (80) appears to hold some promise.

A number of indirect methods of estimating equilibrium adsorption have been proposed and are discussed elsewhere (70). Such methods may be suitable for applications which require only approximate adsorption coefficients; only K_d in the linear equation is usually estimated.

INPUT DATA REQUIREMENTS AND OUTPUT EXPECTATIONS

The previous discussion has focused on dispersion and adsorption; some attention was given to methods that have been used to characterize these properties. Much remains to be done to develop methods that are field oriented in their intent, so that measured dispersion coefficients (or functions) and adsorption parameters will be appropriate for field applications.

For example, recently we found that soil brought to the laboratory in a moist condition adsorbed smaller quantities of two different pesticides than the same soil which was air dried before the adsorption measurement. In most previous studies we have not been concerned about absolute measured values because we were not intending to predict field behavior of the pesticide at a given location or for a given soil condition. But, when field behavior is to be predicted, laboratory measurement conditions should represent field conditions as closely as possible. Thus, if we want to predict the movement of a pesticide in a soil that is normally moist by irrigation, it makes sense to measure adsorption on the moist soil. The same idea would certainly apply to measurement of transformation kinetic coefficients or volatilization parameters.

As mentioned in a previous section, the flux of water in the soil profile, whether down or up, is responsible for moving the pesticide. Poor estimates of water flux will surely result in poor prediction of pesticide movement, except in cases where high adsorption prevents the pesticide from moving. The vertical flux of water in the soil depends principally on soil hydraulic properties and on additions and losses of water at the soil surface, assuming the soil is reasonably well drained. A shallow water table would serve as a water source at the bottom of the root zone and could have important effects on the water flux through the profile over time. Growing plants might have more impact on pesticide mobility in the soil by way of their effect on the direction and magnitude of water flow than by direct uptake of pesticide. Thus, characterizations of hydraulic properties of the soil, including the hydraulic conductivity - water content relationship and suction - water content relationship, and the water inputs and losses over time are as necessary as measuring dispersion and adsorption in a reliable manner. Reliable yet simple methods of measuring hydraulic properties of the soil profile in situ are available (e.g. 81).

Transient water flow has been described successfully on a variety of soils (e.g. 82) with the Richard's equation, which combines Darcy's equation for unsaturated flow with the continuity equation. However, spatial variability in the hydraulic properties over relatively small distances, such as a few meters, can result in very different water fluxes in small areas, let alone large fields (30,60). Variability of field soils is a major consideration when we propose to forecast pesticide mobility. High variability in the flux of water through the soil profile may result in a highly variable depth of pesticide leaching, especially since dispersion and adsorption processes appear to be coupled with water flux. The best strategy in forecasting pesticide movement for areas one hectare or larger may be to obtain measures of central tendency (mean, geometric mean, etc., depending on the nature of the statistical distribution) and variances for each key parameter describing the system, and then determine by statistical techniques the likely variation of the depth of pesticide movement for specified water applications. It is probably unrealistic to expect to model precisely the distribution of pesticide in the soil profile at any given point in a field, but with adequate characterization of an area, it may be possible to predict the mean or geometric mean depth of the pesticide peak and the maximum peak depth anticipated within a specified confidence interval. However, even this level of prediction precision may require more input data than is practical under most pesticide testing programs. It seems there is a real need for public agencies and industry to determine the type of information needed on pesticide mobility in order to protect groundwater quality.

The recent detection of the nematicide DBCP (1,2-dibromo-3-chloropropane) in groundwater pumped from deep wells on Oahu, Hawaii has impressed me that superficial assessments of pesticide mobility for generalized conditions are not adequate. DBCP has been used in pineapple culture for over 15 years, and only recently was the chemical measured in groundwater at a depth exceeding 50 m. I am reasonably confident that given our present knowledge of pesticide-soil-water interactions we could, with the proper input data, determine the likelihood of a pesticide moving 10 to 50 m over a period of years. Exactly how detailed the model must be and how precisely the input parameters must be measured are questions still to be answered.

Leistra et al. (83) have demonstrated that a transport equation similar to Equation [5] in this paper can successfully describe pesticide movement in field soils. They compared predicted and measured propyzamide (herbicide) distributions for five field sites for periods of 56 to 119 days. Although the chemical moved only a maximum of about 0.15 m, the predicted distributions represented measured distributions very well. Subsequently, Leistra and his associates have used transport equations combined with transformation kinetic equations to predict the persistence and mobility of real and model pesticides under a variety of management-soil-environmental conditions (84,85,86,87). Based on limited, yet reassuring validations of model computations with field data, these researchers have used the mathematical models to examine likely effects of various factors on pesticide movement and thereby evaluate various management alternatives. Yet, Leistra and Dekkers (87,88) have emphasized the need for better characterization of (a) water flow, (b) the kinetics of pesticide degradation in the field and (c) adsorption increases over prolonged periods.

The potential for forecasting pesticide mobility in field soils has only begun to be realized. Computers and numerical solutions are now available to solve rather complicated process models that appear to describe the physical and chemical behavior of pesticides in soils. We must decide just how exact predictions need to be, and then proceed to develop improved methods of characterizing key processes and system properties that determine pesticide mobility.

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ADSORPTION OF ATRAZINE BY SOIL ADSORBENTS

by

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Recently much attention has been given to studies on the adsorption of pesticides applied to soil. It is known that up to 80% of the herbicides applied is adsorbed by the top humus horizon, thus almost excluding the movement of herbicides through the soil profile. Most herbicides almost do not undergo degradation in the adsorbed state, and their lifetime in the soil cover significantly increases (2,3).

Herbicides are most often adsorbed by the soil from the soil solution. The intensity of adsorption from a solution on solid adsorbent(soil) at the same temperature,pressure and specific surface depends not only on the nature of adsorbent, but also on that of solute and solvent.

Regularities of the process of adsorption on pure adsorbents are rather adequately studied(I-5). Soil is the most complex natural adsorbent, and this fact is responsible for those difficulties which inevitably occur in studies on the adsorption of various substances by soils(I6,I7,I8). The properties of soil as adsorbent depend on the nature and ratio of clay minerals, quantitative content of the sesquioxides and the form of their existence in the soil,their bonds with the mineral part and organic matter, as well as the amount and nature of soil organic matter(II).

The main most widespread clay minerals entering into the composition of verious soils have different specific surface and substantially differing adsorptive properties. Therefore we began studying the process of herbicide adsorption by soils with the investigation on the regularities of their adsorption on pure clay minerals.

Sesquioxides were shown to be characterized by different adsorptive capacity and selectivity with respect to various herbicides, since the important for adsorptive activity characterisitcs, such as crystalline structure,pore structure and chemical nature of the surface depend on conditions of existence of these sesquioxides.

Several authors studied the behavior of herbicides during their interaction with soil organic matter. Considerably fewer works have been devoted to studying the herbicide adsorption by soils as a whole and the dependence of adsorption isotherm shapes on the properties of adsorbents(I2,I3,I5).

Up to now, there has been neither exact theory of monomolecular adsorption nor general equations of sorption isotherms, though a number of frequently used equations have been derived on the basis of simple models. Among them, the Freundlich equation

$$X = K \cdot C^{1/n}$$

and the Langmuir equation

$$\Gamma = \Gamma_{max} \frac{C}{K+C}$$

are used most frequently in studies of soil adsorption.

The Langmuir adsorption isotherm equation contains two constants: K and Γ_{max}. Constant K is an important characteristic of adsorption system. It is constant for a given adsorption system at a constant temperature and numerically equal to equilibrium concentration at which $\Gamma = \Gamma_{max}/2$. Thermodynamically, K is the measure of adsorption energy.

However, some experimental isotherms of adsorption on solid adsorbents, both porous and nonporous,cannot be interpreted only on the basis of the Langmuir's monomolecular adsorption theory. Further development of the theoretical concepts resulted in the Polanyi's theory, according to which adsorption is determined by Van der Waals forces,their action radius being larger than that of residual valencies in the Langmuir's theory. Due to this fact, adsorption leads to the formation of polymolecular layer rather than is localized in the first molecular layer. Characteristic of this type of adsorption are not the Langmuir isotherms but so-called S-shaped isotherms. In the latter case, adsorption does not cease on the formation of a monolayer but continues until a polymolecular layer is formed. The mechanism of polymolecular layer formation is as yet imperfectly understood, and the theory of polymolecular adsorption in general is still in the semiempirical stage.

Solution adsorption is complicated by the fact that along with adsorption of solute there occurs adsorption of solvent. Therefore various distortions of isotherms of usual type are widespread. Having studied thoroughly the shapes of a great number of solution adsorption isotherms, the authors of (I9) suggested a classification of isotherms which had four main groups(S,Z,H and C) distinguishing by the curvature of isotherms.

All the isotherms were considered by the authors on the basis of different contributions resulted from the interactions: adsorbate-adsorbent, adsorbate-adsorbate and adsorbent-solvent, as well as possible orientations of the adsorbed molecules of adsorbate on the surface of adsorbent.

We made an attempt to establish the dependence of adsorption isotherm shapes on the properties of adsorbents,using as an example atrazine adsorption by soil adsorbents. Many authors studied the adsorption of sym-triazine herbicides by the entire soil (I2,I5,2I), the mineral part of soil adsorbing complex (8,22,6) and its organic part (23,9,20,I0). But it is difficult to generalize this large experimental material, since various authors selected for studying the objects difficult to systematize. Soil organic matter was found to be the main adsorbent of herbicides applied to the soil (7,II,23). Various soils, however, contain different amounts of organic matter represented by different fractions of humus. Therefore various soils should differ in their capeity to adsorb atrazine. In this work, we chose as adsorbents of atrazine the soils with equal and different amounts of humus: top horizons of soddy podzolic soil, chernozem and red soil. Their physical-chemical characteristic is given in Table I.

Table I. Brief physical-chemical characteristic of the adsorbents studied

Adsorbent	Hygroscopicity,%	Clay fraction, %	$pH_{aqueous}$ pH_{water} 5.9	Humus, %	S, m^2/g
Soddy-podzolic soil	I.I3±0.0I	I7±2	6.73±0.05	2.05±0.06	62.4±0.6
Chernozem	3.60±0.07	2I±3	6.30±0.05	4.9±0.05	I32.0±I.5
Red soil	3.67±0.0I	34±3	4.64±0.05	5.0±0.I	200±I0

Mineral part of soils represented by various clay minerals, sesquioxides and their hydrates with different degree of dispersity also has different adsorptive capacity that should affect the total amount of the adsorbed herbicide.

The main purpose of this work was to perform a qualitative and quantitative comparative study of atrazine adsorption by

I) various initial soils;

2) mineral humus-free part of the soils that was obtained through humus oxidation in the initial soil by hydrogen peroxide,using the Hedroits's method:

3) mineral part of the soils without sesquioxides that was obtained through humus oxidation followed by a removal of

sesquioxides by the Jackson's method;

4) humic acids extracted from the initial soils by 0.I normal solution of $NaOH$ followed by a reprecipitation by sulfuric acid and purification by electrodialysis.

Structural and colloidal-chemical properties of the soil sorbents were studied by various methods of physical-chemical analysis.

Mineralogical composition of the studied soddy podzolic soil and chernozem was represented by minerals of the montmorillonite group and hydromicas with an admixture of kaolinite, whereas in the red soil studied, minerals of the kaolinite group and mixed-layer minerals prevailed. The initial soils were composed of clay minerals and organic matter adsorbed extramicellarly on the surface of the mineral part.

Oxidation of organic matter by hydrogen peroxide exposed the surface of clay minerals and sesquioxides. Adsorbents of the mineral part without sesquioxides were represented mainly by a combination of minerals which were a part of the soil adsorbing complex.

Thus, based on the data obtained by various methods of investigation, it can be concluded that the soil sorbents studied differ substantially in their mineralogical composition. This undoubtedly should affect their adsorptive characteristics.

As adsorbate, atrazine has a polar nature, and, therefore, molecular adsorption through the formation of hydrogen or dipole bonds with polar groups and charged surfaces of soil colloids is typical of this substance. In addition, atrazine is a weak base. At $pH = pK$ one half of the molecules of atrazine should exist as cations and be adsorbed by negatively charged soil colloids through the cation-exchange mechanism of adsorption (8).

Atrazine adsorption by the soil adsorbents from aqueous solutions was studied under static conditions at a temperature 20°C, soil-solution ratio I:IO and period of interaction 24 hrs. Atrazine adsorption by humic acids was studied at a temperature 25°C, humic acid-solution ratio I:50 and period of interaction 5 days. Concentration of the atrazine solutions used to study adsorption was determined by spectrophotometry. The amount of atrazine adsorbed by the unit mass adsorbent was determined from the concentration difference of initial and equilibrium solutions.

The results obtained are presented as sorption isotherms in coordinates $\Gamma - Ce$, where Γ is the amount of atrazine adsorbed and C_e is the equilibrium concentration(Fig.I,2,3).

The experimental data obtained are indicative of the complicated character of the interaction of soil with atrazine. Atrazine adsorption by various adsorbents is given by linear and curved isotherms. At low concentrations all isotherms, as a rule, have linear portions, and as the equilibrium concentra-

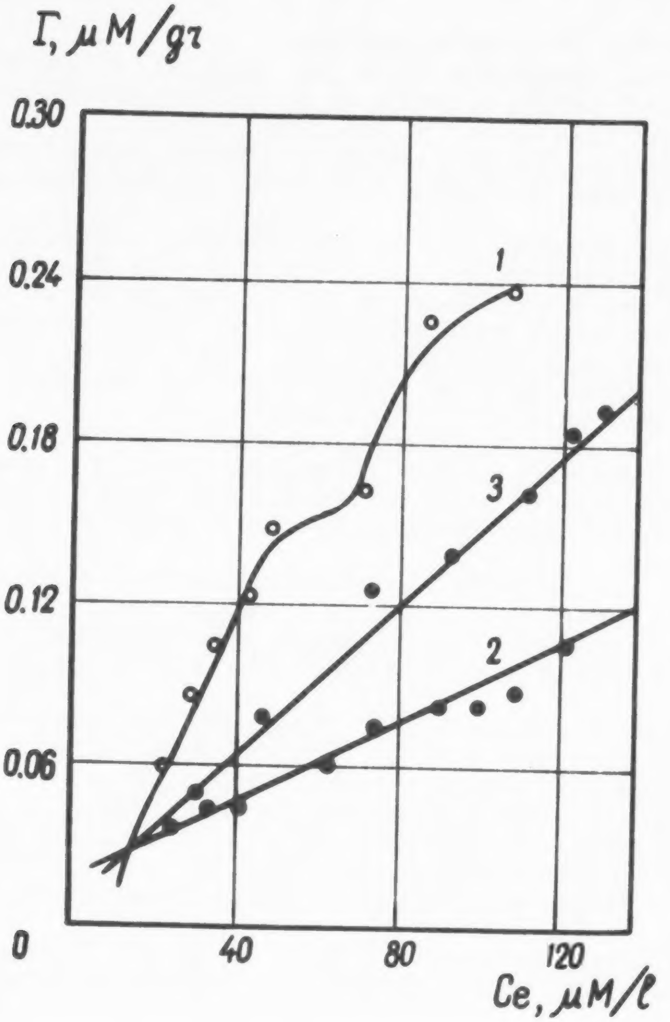

Fig.I. Isotherms of atrazine adsorption by the adsorbents of the soddy podzolic soil:

I - initial soil,
2 - mineral part,
3 - mineral part without sesquioxides.

tion increases, there occur nonlinear portions of the type of the Langmuir curves with saturation or S-shaped curves,according to the Giles's classification (I9) .

All isotherms of atrazine adsorption by the initial soils are two-stage curves with linear initial portions(curve I, Fig.I,2.3).

Oxidation of the soil organic matter by hydrogen peroxide in the initial soddy podzolic soil and chernozem led to a substantial decrease in atrazine adsorption. The isotherm of atrazine adsorption by the mineral part of the soddy podzolic soil is linear over the studied range of concentrations(curve 2, Fig.I).

The isotherm of atrazine adsorption by the mineral part of the chernozem is the two-stage curve with a linear initial portion, the slope of which changed sharply compared to the

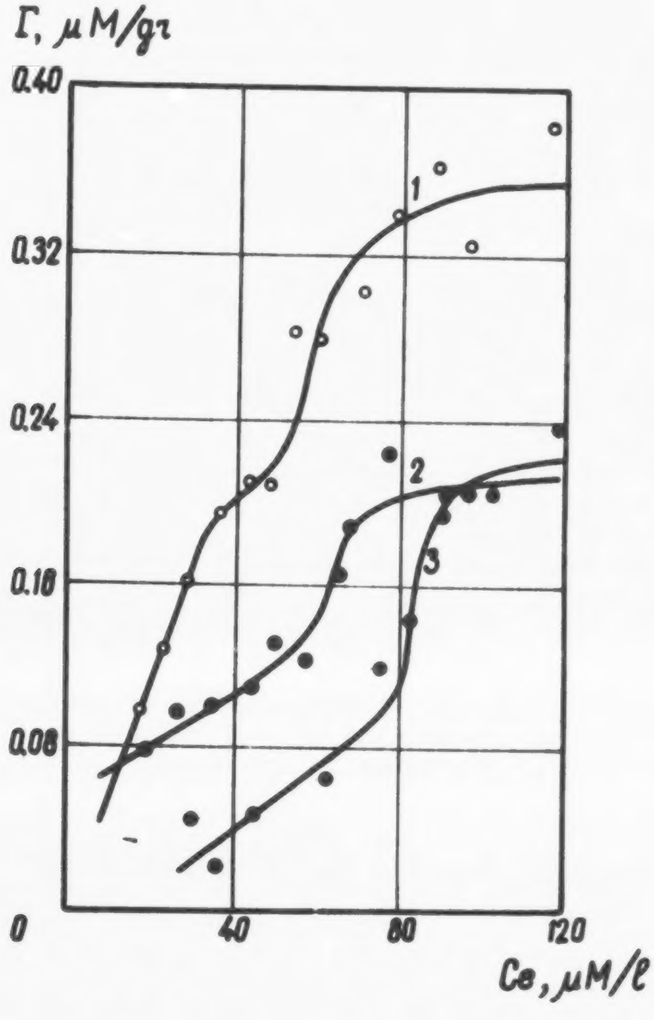

Fig.2. Isotherms of atrazine adsorption by the adsorbents of the chernozem: I,2,3 - same as in Fig.I.

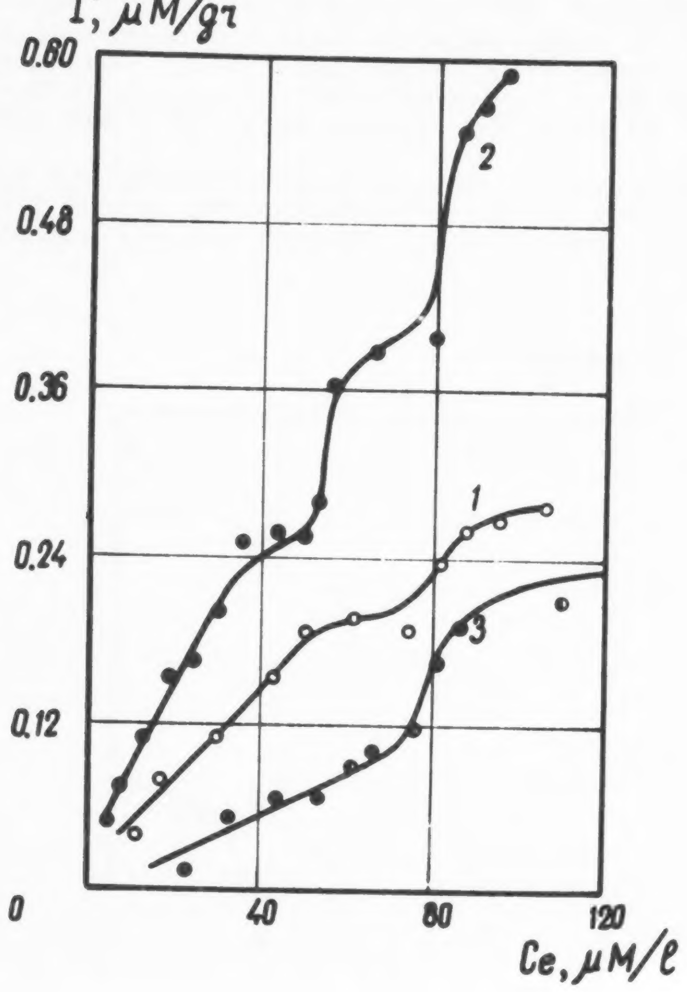

Fig.3 Isotherms of atrazine adsorption by the adsorbents of the red soil: I,2,3 - same as in Fig.I

initial soil (curve 2,Fig.2), and with the second stage of the Langmuir type.

Therefore, the soil organic matter with a high adsorptive capacity was the main adsorbent of atrazine in the soddy podzolic soil and chernozem.

Atrazine adsorption by the mineral part of the red soil sharply increased compared to the initial soil(curve 2,Fig.3). Organic matter of the red soil was represented by alumino- and iron-humus compounds with a fairly high content of aluminium and iron. A major part of humic substances of the red soil were bound to aluminium, since its content in the red soil was 6.I mg equivalent per IOO g, while in the soddy podzolic soil and chernozem only traces of aluminum were detected.

As organic matter was oxidized, alumino-humus compounds were destroyed, and the surface of the mineral part of the red soil covered itself with amorphous aluminum hydroxide which had a large surface and adsorptive capacity, resulting in a sharp increase of adsorption(Fig.3).

The next stage of soil adsorbent treatment was a removal of sesquioxides from the mineral part by the Jackson's method. The removal of sesquioxides caused an increase of adsorption by the soddy podzolic soil and its decrease by the chernozem and red soil. However, a contribution of sesquioxides to the adsorptive capacity of the soddy podzolic soil and chernozem was insignificant. A different situation was observed for the red soil. The removal of sesquioxides exposed the surface of the mineral part of the red soil composed mainly of minerals of the kaolinite group with a small adsorptive capacity, that led into a sharp decrease of adsorption.

Thus, the discussed experimental data indicate that there exists a dependence of the shapes of atrazine adsorption isotherms on the physical-chemical properties of adsorbent(soil), namely, the nature and quantitative content of clay minerals, sesquioxides and soil organic matter.

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STUDY ON PESTICIDE SORPTION UNDER IRRIGATION TO PREDICT AND REGULATE THE PROCESSES OF THEIR MIGRATION IN THE SOIL-WATER SYSTEM

by

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Scientifically valid prediction of the environmental pollution by pesticides and search for ways to prevent undesirable aftereffects of their application are impossible without detailed studies on the processes of toxicant migration in natural landscapes.

The processes of pesticide migration are determined by a number of factors, with sorption playing an important part among them, according to many investigators (3-6). In particular, toxicant transport with water through the soil profile, as well as in irrigation and river networks, and, therefore, the extent of water body pollution by biocides are largely determined by sorption processes.

Favorable conditions for pesticide migration are established under irrigation due to increased water exchange. The main pesticide sorbents in the soil-water system under irrigation are soils, plants and microorganisms.

This paper presents the results of laboratory studies on sorption by soils and microorganisms of some pesticides used in irrigated lands. The obtained data on pesticide interaction with these sorbents can be used for predicting toxicant washout from irrigated lands and working out water-protection measures.

Experiments on soils with a disturbed structure were carried out under static conditions. Sorption of lindane and diuron was studied on the soils of cotton plantations of the Amu Darya-river basin. In studies on the sorption of propanil, its major metabolite 3,4-dichloroaniline(3,4-DCA) and ordram, sorbents were the soils of rice irrigation systems of the Kuban-river basin(Table I).

Table I. Physical-chemical characteristic of sorbents

Soil No.	Name (According to N.A.Kachinsky classification)	Content of fractions, %						Humus, %	Absorbability mg-eq/I00g
		Size of particles, mm							
		I-0,25	0.25-0.05	0.05-0.0I	0.0I-0.005	0.005-0.00I	<0.00I		
		Soils of the Amu Darya Basin							
I.	Loose sand	7.54	87.29	0.33	0.56	I.28	3.00	0.3	2.2
2.	Loamy sand	2.26	80.48	3.50	I.48	2.80	9.48	0.7	5.I
3.	Sandy loam	I.64	69.02	9.32	2.72	6.54	I9.76	0.8	5.6
4.	Moderate loam	I.43	53.2I	I5.24	4.06	I0.52	I5.54	I.0	6.6
5	Gray-brown sandy loam	0.52	II.83	I6.6I	I5.44	28.92	26.68	I.I	I3.6
		Soils of the Kuban Basin							
6	Loose sand		94.I	2.2	0.3	0.3	3.I	0.05	0.98
7	Loamy sand	0.I	58.7	26.5	I.8	3.7	9.2	0.I5	8.42
8	Light clay	0.3	0.4	3I.5	I4.7	I7.6	35.5	I.0	25.60
9	Meadow-chernozemic clay loam	0.I	2I.8	3I.2	7.6	II.9	27.4	2.7	27.30

Preliminary experiments revealed the optimum ratios of solid to liquid phases at which the processes of sorption were studied. Then the kinetics of sorption equilibrium establishment was studied, i.e. the time variation of sorbate concentration in the aqueous phase was regulated. As the equilibrium had been attained, sorption isotherms were measured.

The process of organic matter sorption by soils from a solution is a very complex phenomenon. The behavior of organic matter in the soil-water system is determined by its chemical composition, the nature of functional groups,properties of a sorbent and a number of external physical-chemical factors. We did not separate the influence of individual factors: soil was not divided into fractions; organic and mineral components were not isolated from it; and the value of pH of the water-soil suspension was close to the neutral one.

Kinetic curves show an increase in the amount of the sorbed substance with time and an asymptotic approximation to the equilibrium one. A state of the system in which any change of the concentration in the aqueous phase of the substance studied stopped was taken as the sorption equilibrium. Analysis of the kinetic sorption curves of lindane, diuron, propanil, 3,4-DCA and ordram shows that within the systems studied, the sorption equilibrium is reached in a few minutes after the beginning of phase interaction, irrespective of the nature of compound, its initial concentration and soil properties. Reaching the sorption eqilibrium in such a short time is indicative of a prevailing physical interaction between sorbate and sorbent.

The study of the relationship between the amount of adsorbed substance and the equilibrium concentration at a constant temperature enabled us to plot sorption isotherms. As a result of mathematical processing of the experimental data, it was found that the isotherms of sorption by soils of the above pesticides can be adequately given by Freundlich equation:

$$\Gamma = k \cdot C_e^{I/n} ,$$

where Γ is the specific absorbability of sorbent,mg/kg; C_p is the equilibrium concentration of sorbate in the solution, mg/l, k and I/n are the experimental constants of sorption isotherm.

The corresponding constants were calculated(Table 2).

One can see from the isotherms of lindane and diuron sorption by soils that sorption is strongly dependent on pesticide concentration in the aqueous phase. In the range of the concentrations studied, we did not observe complete saturation of sorbents, with the exception of sand. Relative absorbability of soils No.I-5 decreases in the following order: gray-brown sandy loam - moderate loam - sandy loam - loamy sand - sand. As seen from Table I, humus content in the soil sorbents decreases from I.I% to 0.3%. Larger amounts of pesticides were sorbed by soils with larger content of organic matter. In addition, the content of clay fraction in the same row decreases

Table 2. Constants of Freundlich equation

Pesticide	Soil No. (Table I)	k	I/n
Lindane	I	0,43	0,40
	2	0,76	0,39
	3	I,47	0,88
	4	I,52	0,84
	5	2,57	0,54
Diuron	I	0,5I	0,50
	2	0,60	0,77
	3	0,96	0,72
	4	I,2I	0,59
	5	I,39	0,82
Propanil	6	0,I7	0,73
	7	0,68	0,4I
	8	9,32	0,53
	9	II,27	0,48
3,4 DCA	6	0,I0	0,87
	7	0,60	0,32
	8	7,6I	0,74
	9	8,55	0,7I
Ordram	6	0,05	0,73
	7	0,07	0,32
	8	4,3I	0,9I
	9	5,28	0,7I

from 26.68% to 3.00%,i.e. specific absorbability of soils with respect to lindane and diuron increases, as the content of clay fraction in them rises.

Relative absorbability of soils No.6-9 decreases in the following order: meadow-chernozemic clay loam - light clay - loamy sand - sand. In this row, humus content (Table I) decreases from 2.7% for meadow chernozemic clay loam to 0.05% for sand. Thus, absorbability of soils No.6-9 with respect to propanil, 3,4-DCA and ordram obviously correlates with humus content in them. At the same time, the content of clay fraction decreases in a different order: light clay-meadow chernozemic clay loam - loamy sand - sand. The first two links in this chain do not provide correlation with absorbability. Therefore organic colloids apparently play a more important part in sorption of propanil, 3,4-DCA and ordram than minerals entering into the composition of soils.

From the results of the studies conducted it can be concluded that organochlorine pesticides are capable of being sorbed by the soils of cotton fields to a greater extent than herbicides-derivatives of urea. Amides of propionic acid are sorbed by the soils of rice checks to a greater extent than thiocarbamates.

Consequently, derivatives of urea should have higher migration capacity under conditions of cotton fields than organochlorine pesticides, whereas soil herbicides of the thiocarbamate group possess higher migration capacity under conditions of rice irrigation systems than contact herbicides of 3,4 - dichloropropionanilide group.

The processes of pesticide sorption by microorganisms were studied on propanil - a contact herbicide widely used in rice growing. As the main part of aquatic microbiocenosis is represented by bacterial forms, the above processes were studied on individual species of the main systematic groups of bacteria (representatives of Pseudomonas, Micrococcus, Bacillus, Achromobacter and other genera). Microorganisms were cultured on a thick nutrient medium during two days at a temperature 27°C. Bacterial cells washed off the nutrient medium were suspended in a small amount of water and transferred to experimental vessels containing herbicide solutions. At the end of the experiment the microbial biomass was separated from the liquid by centrifugation.

It was found that bacterial cells are capable of sorbing propanil. At the same time, a portion of the toxicant penetrated into a cell. As it was difficult to make a distinction between these processes, we determined mainly the net effect of propanil concentration decrease in water when in contact with bacterial cells(Tables 3 and 4).

Increase in propanil concentration in the medium at a constant quantitative content of bacteria promotes increasing value of toxicant sorption and uptake per I kg of biomass to a certain range of herbicide concentration, after which the saturation is attained(Table 3).

Increase in biomass promotes more intensive decrease in toxicant concentration. However, after reaching some critical value sorption decreases again (Table 4). This is likely accounted for by the aggregation of individual cells at their too high concentration in the medium, which decreases specific surface and accessibility of the active centers. Equilibrium

Table 3. Influence of propanil concentration in water on its sorption and uptake by microorganisms Pseudomonas sp. at a biomass concentration of 2.5 g/l

Concentration of herbicide, μg/l		Γ,mg/kg
initial	steady-state	
I35	I05	I2
2I0	I35	30
340	248	37
554	452	4I
680	570	44
I300	II68	45

Table 4. Influence of bacterial biomass concentration on propanil sorption and uptake at its initial concentration of 665 μg/l

Biomass, g/l	Ce, μg/l	Γ,mg/kg
I,0	655	I0
2,5	570	38
5,0	455	42
I0,0	5I5	I5
20,0	565	5

state in the experiments to study propanil sorption by bacterial biomass was reached approximately in 2 hours.

We observed certain differences in the capacity of microorganisms to sorb and accumulate propanil, depending on their species characteristics. Gram-negative bacteria can sorb a toxicant better than gram-positive ones. Despite the small absolute values,the revealed capacity of microorganisms to sorb pesticides is apparently of great importance for the redistribution of these substances in the aquatic environment, considering a substantial uptake of bacterial biomass by invertebrates.

The studies conducted support the feasibility of using the sorption processes in the complex of measures aimed at preventing natural water pollution by pesticide residues. In particular, an increase in the absorbability of soil-forming rocks with respect to these substances should promote a decrease in the level of drainage water pollution. Soil-forming rocks which contain, as a rule, trace amounts of humus substances can not hold completely pesticides and their transformation products transported to drainage network at a short distance of water traveling.

As it was proved experimentally that soil organic matter plays a leading part in the sorption of herbicides used in rice growing, we proposed a bed-type screen (2) made of loam with humic additions. The screen is an interlayer placed under the root layer over the entire area of check floor or its part to localize these herbicides within the rice check. Salts of humic acid form with clay particles a stable clay-humus complex which actively absorbs herbicides. As substances of humic origin, one can use humus, peat, brown coal treated properly by alkali agents to extract salts of humic acids. Increase in absorbability of the interlayer can be attained by introducing lignin-containing substances into its composition (I). We found a high absorbability of lignin-containing substances with respect to herbicides. In addition, lignin is one of those compounds which are most resistant to enzymatic decomposition and converts to humus substances in the process of slow degradation. Due to these properties of lignin-containing substances the interlayer proposed can function for a long time.

Testing the effectiveness of application of the loam screen with humic additions to reduce washout of herbicide residues in drainage waters that was conducted under field conditions in the Krasnodar Territory and South Ukraine showed that the measure proposed promotes almost complete absorption of propanil and ordram, as well as 3,4-DCA which is formed during propanil transformation. Microbiological analysis of the soil layer above the screen and its middle part showed that introduction of humus substances into the composition of the interlayer promotes an increase in its biological activity sufficient for detoxication of the toxicants absorbed during the growing season.

The screens outlined above are of interest for those areas of irrigated agriculture with high water permeability where drainage runoff plays an important part in pesticide washout.

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CHARACTERISTICS OF SOIL DEGRADATION STUDIES FOR PREDICTING PESTICIDE BEHAVIOR

by

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ABSTRACT

Degradation rates of chemicals in a major environmental compartment like soil are key ingredients of any hazard evaluation process. Therefore, a primary goal of soil degradation studies is to provide a general characterization of the degradation rates of chemicals in soil. Since these rates come from interaction between chemical, soil, and climate; there must also be assessment of soil type, soil moisture, and soil temperature on the degradation process. Factorial statistical designs are useful in designing these experiments because they allow maximization of information for minimal amount of effort. Data from such studies are appropriate for modeling environmental fate of chemicals in standard environments representing distinct land resource regions.

Sooner or later pesticides come in contact with soil. They can reach soil in a variety of ways --- through direct application during spraying or soil treatment, and more indirectly through washoff of foliage or deposition from atmospheric fallout. If we are to have knowledge of the environmental fate of pesticides, then we must know something about their degradation in soil.

It is very difficult to carry out degradation experiments in the totally uncontrolled environment of a real field situation.Perhaps the most successful method of learning about pesticide degradation is to carry out rigidly controlled experiments in the laboratory. These involve the incubation of treated soil in suitable containers, which in turn are placed in controlled temperature chambers during their incubation. In this manner one learns about the degradation of pesticides in soil under well-defined conditions. This information becomes quite appropriate for evaluation of pesticide behavior.

In our laboratory we have chosen the highly controlled laboratory experiment rather than the field approach to study chemicals in soil. The studies are designed to accomplish two things. The first is to learn about the degradation of chemicals in soils in a very general fashion, and to learn how the degradation might vary from one soil to another. The second deals with the effect of different soil climates on the breakdown of pesticides in soil. If studies are conducted in the right manner, this will reveal the fate of a pesticide when added to soil.

Many types of systems have been used to incubate chemicals in soil. One of the earliest is the perfusion set-up like that in Figure 1. Water

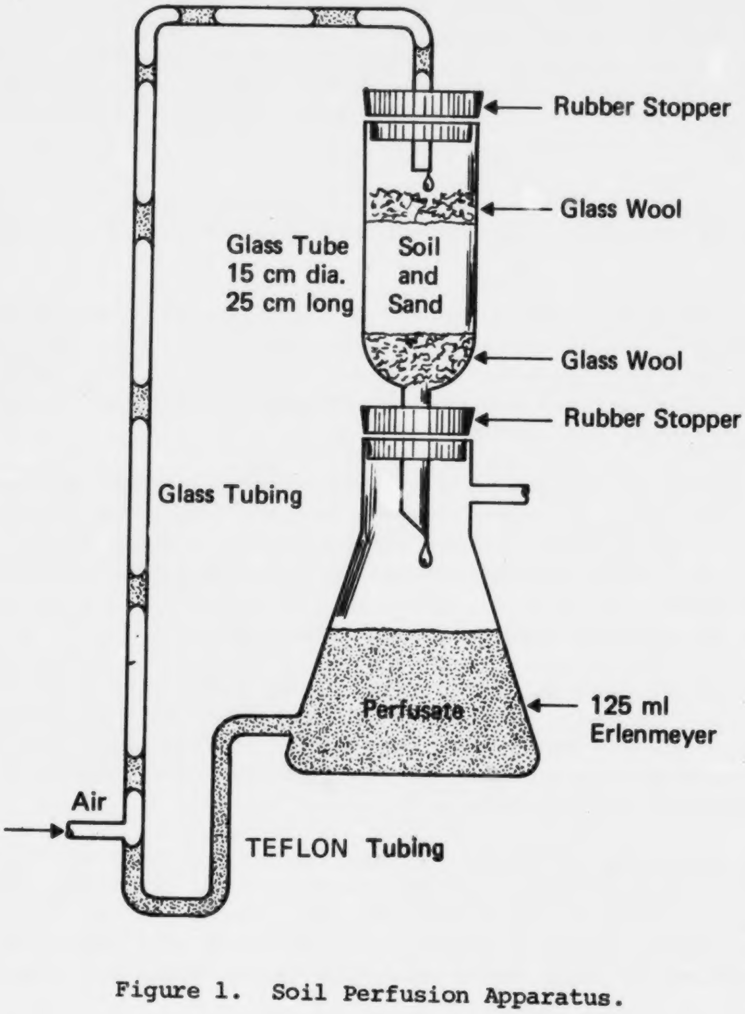

Rubber Stopper
Glass Wool
Glass Tube
15 cm dia.
25 cm long
Soil
and
Sand
Glass Wool
Rubber Stopper
Glass Tubing
Perfusate
125 ml
Erlenmeyer
Air
TEFLON Tubing

Figure 1. Soil Perfusion Apparatus.

solutions of pesticide generally are pumped through a column of soil. This particular system uses an air pump to recycle the perfusate, but other types of pumps have also been used. The fate of the pesticide is followed by periodic analysis of the water solution.

Perfusion systems are best suited for microbial enrichment studies. They are not easily adapted to measurements of real soil degradation rates, or used easily with volatile or water-insoluble chemicals. Other incubation systems perhaps adapt much more readily to the purposes of predicting pesticide behavior.

One such system is the continuous aeration system described by Kearney and coworkers (1). A glass container with treated soil is fitted with a two-hole rubber stopper. Air at low flow enters through one hole and exits from the other through two traps. The first trap is a polyurethane foam plug that collects pesticide in the air stream as a result of volatilization. The second trap is sodium hydroxide for trapping carbon dioxide or other acidic gases produced during the degradation. These traps allow complete accounting of all added pesticide ---- an important objective in soil degradation studies.

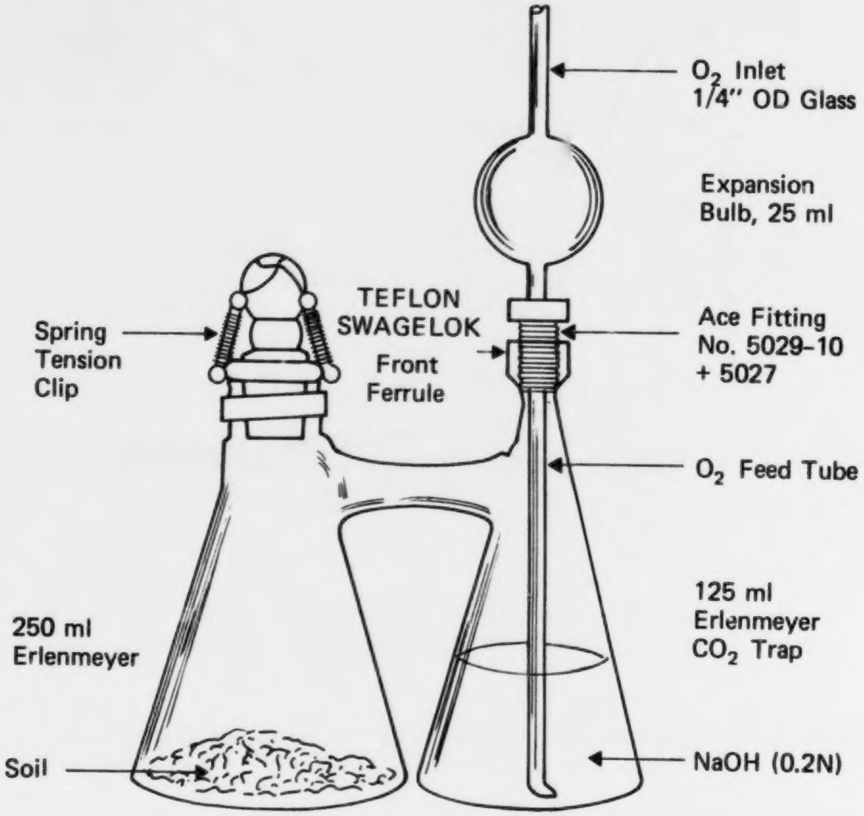
One requirement of this system is that corrections must be made for volatilization if one wishes to characterize degradation of chemicals in soil.

Another kind of incubation system is a totally enclosed one designed by Bartha and Pramer (2). It consists of two compartments --- one for treated soil and the other for concentrated sodium hydroxide to trap carbon dioxide. Because of its design, fresh air must be manually introduced periodically to maintain oxygen inside the system.

Our laboratory re-designed the two-compartment system to that shown in Figure 2. We removed all rubber stoppers and replaced them with glass so that pesticide would not be absorbed by the rubber present in the original design. Then the sodium hydroxide trap was made larger to accommodate the use of dilute caustic solutions. These do not cause the drying of the soil observed with the concentrated solutions used originally.

Finally, we provided automatic aeration by connecting each unit to an oxygen manifold. The units were isolated from each other by delivering the oxygen through a glass tube extending into the caustic solution. An expansion bulb was provided to protect the manifold from the caustic in the event of pressure increase in the unit.

The same apparatus is used if we wish to examine anaerobic soil degradation. Enough water is added to provide a layer over the soil. The flask atmospheres are changed to pure nitrogen gas; the units are not connected to the oxygen manifold. Alfalfa ground to a fine size is added to provide energy for driving the soil redox potential to the anaerobic state.


O_2 Inlet
1/4" OD Glass
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Clip
Ace Fitting
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+ 5027
O_2 Feed Tube
125 ml
Erlenmeyer
CO_2 Trap
250 ml
Erlenmeyer
Soil
NaOH (0.2N)

Figure 2. Closed System Apparatus For Aerobic Incubation Of Chemicals In Soil.

A typical experiment is prepared by addition of pesticide to the soil in water or in no more than 250 µl of acetone. The soil is then mixed thoroughly. Water is added to bring the soil to a desired moisture and the soil is mixed again. Finally, caustic is added to the carbon dioxide trap, and units are assembled in constant temperature chambers for subsequent incubation. There are several chambers and each is set at a different temperature in order to study temperature effects on the degradation.

Typical sampling periods are 0, 7, 14, 28, 56, 100, 200, and 300 days.

The results from these studies present degradation patterns like those given in Figure 3 (3). The degradation kinetics of the parent molecule is displayed; the patterns of breakdown product accumulation and decline are observed.

Nearly all of our work is with carbon-14 labeled material. Balance sheets for recovery of total radioactivity with our incubation system show good accountability of all activity (Table I).

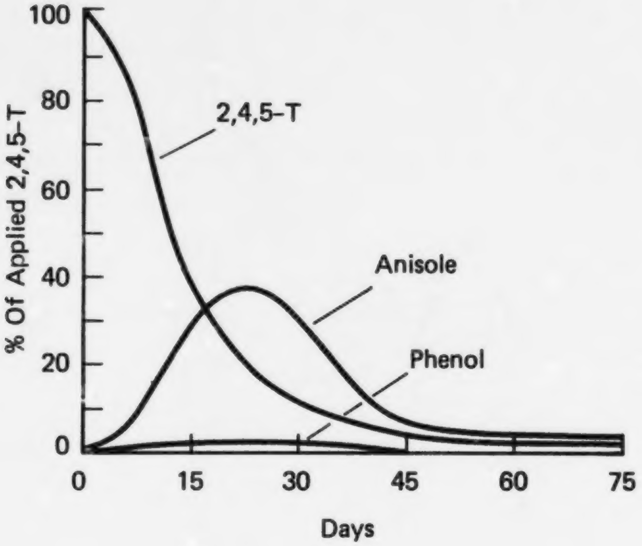


Figure 3. Example Of Information Obtained From Soil Degradation Studies.

Table 1. Typical Accountability Of Radioactivity.

Average Recovery	98.6%
Standard Deviation	4.8
Number of Samples	209

As indicated earlier, our experiments have two purposes. The first deals with characterizing the general rate of degradation taking place in soil. In order to do this in a meaningful fashion, however, we concluded there must be studies with several soils incubated under standard conditions of incubation. Table 2 cites the conditions often used by many researchers and which have been adopted by us.

You may ask why it is necessary to examine the degradation of pesticides in more than one soil, as specified in Table 2. It is because soils differ in their ability to degrade chemicals. To illustrate this, consider the data presented in Table 3. Table 3 was derived from the literature (4) and lists the variability in soil degradation rate for a variety of pesticides, each of which was studied in a number of soils under identical incubation conditions. As you can see the variation in rate of degradation ranges from two-fold to 80-fold --- the average equaling more than 10-fold.

Table 2. Standard Incubation Conditions For Soil Degradation Studies.

Number of Soils	6-10
Incubation Temperature	25°C
Incubation Moisture	75% 1/3 Bar

Incubation in the Dark

Table 3. Variation In Rate Of Degradation Among Surface Soils For Several Pesticides.

Chemical	# Soils	Range of Observed Differences Among Soils
Crotoxyphos	3	36X
Linuron	4	2X
Methomyl	2	2X
Glyphosate	4	19X
Aldicarb	2	2X
Carbofuran	4	25X
DIAZINON	4	2X
Thionazin	4	7X
Methidathion	4	3X
Nitrilotriacetate	11	80X
Nitrapyrin	10	6X
Picloram	13	19X
Propyzamide	5	2X

Note: Only experiments that expose soils to chemicals under identical conditions are cited.

This difference cannot be predicted from any known soil properties. Therefore, a number of soils must be studied if we are to evaluate the behavior of chemicals in soil.

Our soils also are collected and stored by a standard procedure. They are taken from the top 10 cm of an area approximately 9 square meters in size. They are stored in polyethylene bags at 4°C for no longer than one year before use. They are never allowed to air dry since this might kill key microorganisms and alter the soil's degradation characteristics.

It is interesting to contemplate how data from such standardized experiments as these might be used. One such use may be for comparison of soil degradability among pesticides. Since these studies provide degradation rates from a variety of soils all incubated under the same standard conditions, it is possible to compare average degradation rates in the manner shown in Table 4. Pesticides degrading the fastest are at the top of the list --- those that are stable are found at the bottom.

Table 4. Ranking Of Pesticides According To Rate Of Degradation In Soil.

Pesticide	Days for 50% Degradation
Malathion	1
2,4-D	4
Alachlor	7
Nitrapyrin	10
Parathion	15
Dicamba	20
DIAZINON	30
Chlorpyrifos	60
Atrazine	130
Monuron	170
Diuron	200
Lindane	600
Dieldrin	1000
Heptachlor	2000
DDT	3800
Endrin	4300

Average degradation rates can be used for other purposes. They can be categorized so that one can describe the soil stability of a chemical as being "very low" or being "very high". In essence, they provide descriptive terms that can be used in discussions of soil behavior (see Table 5).

Table 5. Categorization Of Soil Degradation Rates For Pesticides.

Category	t/2, Days
Very Low	< 15
Low	15-60
Medium	60-180
High	180-360
Very High	>360

So to summarize the first part of our soil degradation studies --- their aim is to demonstrate the kinetics of degradation in a variety of soils under standard conditions. An average time for 50% breakdown is determined, and this value then becomes a general measure of a pesticide's degradation in soil.

If you recall, the second main objective of soil studies carried out by us is to determine the effect of soil climate on rate of degradation. We present aspects of these studies for your perusal.

The studies essentially relate to how soil climate and initial soil concentration of pesticide might change the rates of degradation. In addition to the effects of soil already observed in the first part of the study --- the soil temperature, the moisture, and the starting concentration of pesticide --- all have influence on degradation. These too must be evaluated for assessment of pesticide behavior in soil.

It is not easy to examine several parameters in a single experiment without being overwhelmed by the number of necessary samples. To solve this problem the experimenter can utilize the efficiency of a statistical factorial design. In our laboratory we chose a modified central composite design described by Cochran and Cox (5). Values of temperature, moisture, and initial soil concentration used in the design are shown in Table 6.

The actual design can be viewed as if the combination of incubation parameters described a cube (see Figure 4). Two soils are used and both occupy the position shown in the center of the cube. In other words, both soils are incubated under identical conditions of 25°C, 50% of 1/3 Bar, and

1 ppm initial concentration of pesticide at this point. The corners of the cube locate the incubation extremes --- the points in between establish the surfaces between the extremes.

Table 6. Factorial Design Values For Studying Effects Of Moisture, Temperature, And Initial Concentration On Rates Of Degradation.

Temperature, °C	15, 25, 35
Moisture, % 1/3 Bar	Air Dry, 25, 50, 75, 100
Concentration, ppm	0.1, 1.0, 10

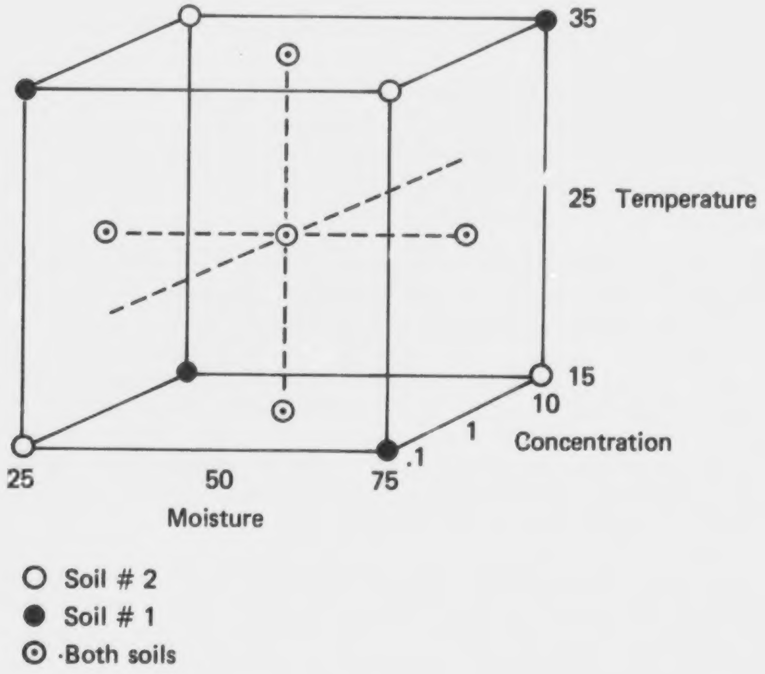
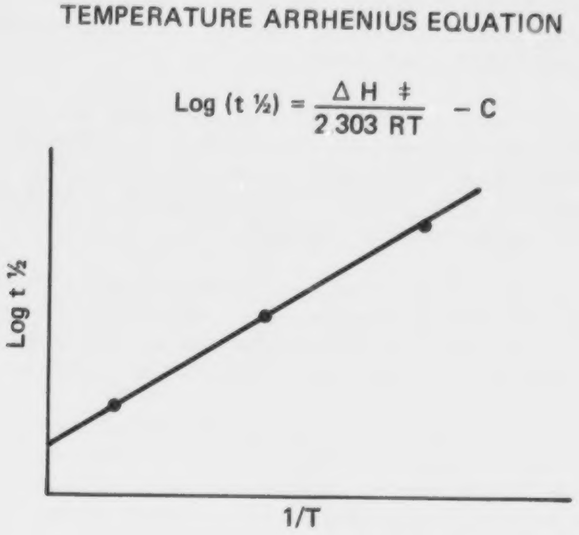

35
25 Temperature
15
10
1
.1
Concentration
25
50
75
Moisture
○ Soil # 2
● Soil # 1
⊙ Both soils

Figure 4. Schematic Representation Of Central Composite Factorial Design.

The final outcome of this design is the development of mathematical expressions describing the relationships of temperature, moisture, and initial concentration to rate of degradation. Figure 5 shows the temperature effect from studies with one of our chemicals. The relationship is described quite well in soil by the well-known Arrhenius Equation.

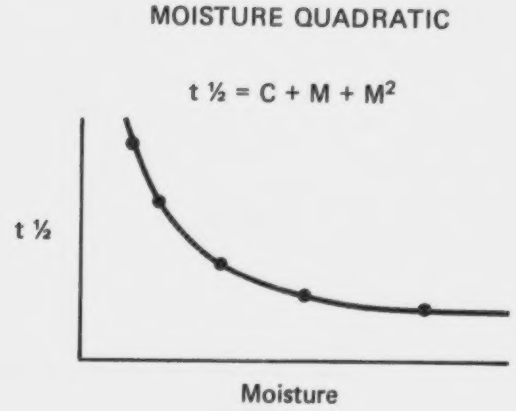


TEMPERATURE ARRHENIUS EQUATION

$$\text{Log}\,(t\,½) = \frac{\Delta H^{\ddagger}}{2.303\,RT} - C$$

Figure 5. Relationship Between Temperature And Rate Of Degradation In Soil.

Figure 6 presents the moisture expression we have observed. It appears quadratically related to rate of degradation but this has not been verified extensively.



MOISTURE QUADRATIC

$$t\,½ = C + M + M^2$$

Figure 6. Observed Relationship Between Soil Moisture And Rate of Degradation in Soil.

The expression for initial concentration of pesticide and rate of degradation appears to be somewhat logarithmic in nature (Figure 7). Again, we do not have a great deal of evidence for this relationship, and future work may show different patterns.

At any rate, it is possible to assemble the information from the factorial design into a single expression. With this equation one can then estimate rate of degradation from knowledge of soil temperature, soil moisture, and initial concentration of pesticide.

How might this information be used? One obvious way is for prediction of behavior of a pesticide at specific locations. If the climatic pattern of a location is known throughout an event, then the fate of a pesticide at the site can be modeled during that event. This provides knowledge of environmental fate needed for assessment of hazard.

Another use of perhaps even greater utility relates to the modeling of pesticide behavior in standard environments. We would like to discuss briefly the concept of standard environments and consider their future role in the process of modeling environmental fate of pesticides.

Our laboratory has become interested in building standard descriptions of environments that would represent regions of our country. We are utilizing an existing scheme described by Austin (6) that develops regions in the United States on the basis of soil type, topography, climate, and land use. We chose several regions considered to be of greatest importance and are now assembling representative physical descriptions of these regions for use in assessment of pesticide behavior. The task is not yet complete, but for those who may be interested the current efforts are described in (7).

We believe the use of standard descriptions of representative regions will be the way of the future for evaluating the behavior of pesticides.

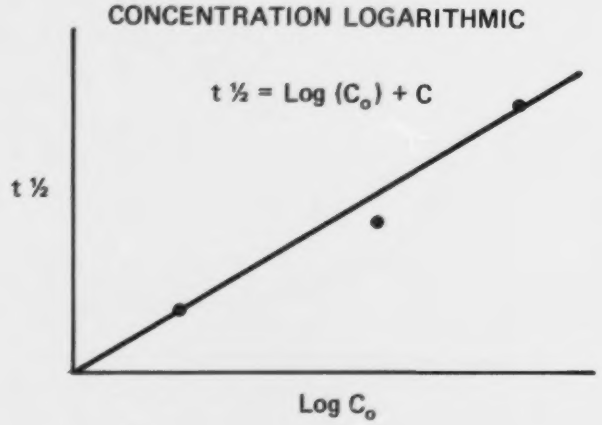


Figure 7. Apparent Relationship Between Initial Concentration And Rate Of Degradation In Soil.

Their advantage is the ready availability of the vast physical environmental data required by any model describing environmental fate. It would not be necessary to go through the expensive process of actually measuring these physical characteristics whenever a modeling exercise was undertaken.

To attempt modeling of environmental fate of any type, however, we wish to re-emphasize that there must be knowledge of how climatic factors influence the degradation of pesticides in soil, and how different soils themselves impact on this degradation.

So in summary, soil degradation studies have two basic goals if they are to be used in the evaluation of pesticide behavior. The first is to provide a general characterization of degradability from experiments with several soils at standard incubation conditions. The second is to quantitate the effects of environment on degradation. This quantitation then can be used to model pesticide behavior in a wide variety of environments.

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TRANSLOCATION AND TRANSFORMATION OF PESTICIDES IN SOILS AND PLANTS

by

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Ecological approach to chemical plant protection is associated largely with a thorough study of the behavior of chemicals applied. An understanding of this problem permits, on the one hand, to achieve the required effect and, on the other hand, to reduce as much as possible a detrimental influence of chemicals on the useful species of organisms,prevent negative effects of sanitary-hygienic nature, and eliminate environmental pollution. This problem can be solved with regard to the toxicological and physiological properties of those pesticide chemicals that are widely used in agriculture on the global scale, primarily to their toxicity to warm-blooded animals, and persistence in soils, aquatic environments and plants. Accordingly, the assortment(list) of pesticides of domestic manufacture and ,in particular, that of the last few years,has been subjected to constant changes. Table I shows the data on the change in the assortment of insecticides and acaricides of various chemical groups. It is seen from the table that the application of arsenic-containing and inorganic chemicals since I960 has sharply decreased (from 4 items to I), whereas that of organophosphorus chemicals has considerably increased (from 6 items to 29). The assortment of insectoacaricides has increased recently due to the included chemicals from other groups, such as pyrethroids, nitrogen-containing compounds, carbamates, etc.

In the last few years the assortment of chemicals increased due to new less toxic pesticides. For example, the mean danger class for the insectoacaricides recommended in I980 was 2.69, whereas in I960 it was I.69. It should be noted that this index incorporates all possible manifestations of danger of the chemicals,i.e. not only an acute toxicity but also potential chronic, mutagenic, teratogenic and other side effects.Compared

Table I. Changes in the assortment of insecticides and acaricides in the Soviet Union in the period from I960 to I980 (the number of items of the active agents of insectoacaricides)

Groups of compounds	I960	I970	I980
Synthetic pyrethroids	-	-	5
Arsenic-containing and inorganic compounds	4	2	I
Organochlorine compounds	5	9	I0
Organophosphorus compounds	6	I7	29
Carbamates	-	I	3
Nitrogen-containing compounds	I	3	3
Other compounds	4	4	9
Total	20	36	60

to I960, the index of mean toxicity to warm-blooded animals for the active agents of insectoacaricides increased fivefold and amounted to 990 mg/kg instead of 220 mg/kg. Specific toxicants with LC_{50} over I000 mg/kg account for about 30% of the recommended compounds. Among the latter there are highly selective insectoacaricides, yet the great majority of them are highly toxic to most species of insects.

Translocation and transformation of pesticides in the area of their application, that is a combination of migration processes and quantitative-qualitative changes of the chemicals, ultimately determines tactical approaches to their use in specific agrocenoses.

The All-Union Research Institute for Plant Protection carried out extensive studies on the translocation of insectoacaricides affected by a variety of factors of biological and nonbiological nature, and established regularities and relations determining the behavior of chemicals in environmental objects. The facts revealed enabled the "mild" norms to be provided for the use of chemicals for a number of crops, which in turn aided in reducing environmental pollution by pesticides. Thus, as a result of studying the behavior of insecticides in plants and soils under conditions of the Non-Chernozemic zone of the Soviet Union, the amount of dehydroheptachlor applied as sprays to control potato beetles was reduced threefold. When using the granulated insecticides bazudin (diazinon) and dursban (chlorpyrifos) in the Volgo-Vyatskii region to protect corn and potato plants against wireworms (Agriotis sputator L.), it is recommended to apply these chemicals differently with regard to the type of soils. It is seen from Table 2 that LC$_{50}$ for wireworms in the podzolic soil can be reached at a lower concentration of the chemicals(0.3-0.4 mg/kg),compared to the chernozem(I.2-2.4 mg/kg). This regularity enables one to reduce the rate of insecticide application in the podzolic and soddy podzolic soil by over one half, compared to the chernozemic soil.

Table 2. Content of organophosphorus insecticides in various soils and their toxicity to wireworms Agriotis sputator L

Soil type	Applied, kg/hectare	Insecticide content in the soil three days after its application, mg/kg		LC$_{50}$ for wireworms, mg/kg of soil
		Bazudin (Diazinon)	Dursban (Chlorpyrifos)	
Podzolic soil	0.6 0.8	0.52 0.7I	0.55 0.80	0.3-0.4
Soddy podzolic soil	I.2 2.5	I.09 2.33	I.I5 2.40	0.6-I.I2
Gray forest soil	I.6 2.5	I.44 2.32	I.55 2.48	0.7-I.60
Chernozem	2.5 5.0	2.4 4.8	2.48 4.92	I.2-2.4

As agricultural crops are protected against pests,pesticides reach the soil either by direct application or indirectly. We pointed out earlier that when spraying plants, one can find a small amount of toxicants directly in the soil. This fact was supported by our further experiments(Table 3). While treating well-developed cotton or potato plants in June-July, we found on the day of treatment less than 0.2 mg/kg of the insecticides in the soil and up to 22 mg/kg in the plants, whereas in case of cabbage plants the content of insecticides in the soil was about I.2 mg/kg. The above amounts of the chemicals permitted for use can completely decompose for 5 to IO

Table 3. Distribution of insecticides in plants and soils, when spraying agricultural crops (on the day of treatment)

Insecticide	Crop	Rate of application, kg/hectare with respect to the active agent	Insecticide content, mg/kg	
			in plant	in soil
Valekson O,O-Diethyl-thiophoshoryl-O-(-cyanobenzaldoxime)	Tomatoes	0.7	3.9	0.I
	Potatoes	0.7	5.0	not detected
	Cabbage	I.2	I.8	I.2
Bazudin (Diazinon)	Cabbage	I.5	2.49	I.I
Ambush (Permethrin)	Cotton	0.2	4.0	0.0I
Zimbush -cyano-3-phenoxybenzyl-2,2-dimethyl-3-(2,2-dichlorovinyl)-cyclopropane carboxylate	Cotton	0.08	0.6	0.002
Actellick (O,O-Dimethyl-O-(2-diethylamino-6-methylpyrimidyl-4)-thiophosphate	Tomatoes	3.0	7.3	0.I
Thiodan (Endosulfan)	Cotton	I.0	22.0	0.2

days.

Granulated insecticides, both soil-incorporated and surface-applied at the moment of planting agricultural crops, cause much anxiety as soil pollutants. Table 4 presents data on the persistence of granulated insecticides at a level of 50% of the initial amount for a number of agricultural crops. As seen from the table, the chemicals remain at the above level in the soils from 25 to I20 days, with the exception of a granulated phosphamide which can be washed out rather easily by rains or during heavy watering.

Table 4. Persistence of granulated insecticides in the soil for various agricultural crops

Insecticide	Crop	Rate of application, kg/hectare	Persistence (50%) of insecticide in soil, days
Bazudin I0% granulated	Alfalfa	5.0	30-75
	Sugar beets	5.0	50-I00
	Corn	5.0	28-75
	Cotton	5.0	40-90
Volaton, 5% granulated	Potatoes	2.5	25-60
	Corn	2.5	25-60
BHC, 2% granulated	Sugar beets	I.0	80-I20
	Wheat	I.0	70-I00
	Corn	I.0	40-80
Dursban, I0% granulated	Potatoes	5.0	60-90
Phosphamide (Dimethoate), I.6% granulated	Peas	0.5	I5-70
	Sugar beets	2.0	70-I00

We have shown that the persistence of granulated chemicals in soil depends on the ability of plants to remove a toxicant from soils and metabolize it to simpler compounds. Thus the lowest level of bazudin in the soil is typical of alfalfa and corn, compared to cotton or sugar beets. It should be noted that other chemicals also persist for a longer time in the fields sowed with sugar beets.

Studies on the dynamics of chemicals depending on various methods of using granulated toxicants showed that soil-incorporated insecticides decompose more rapidly than surface-applied ones(Table 5). It is seen from the table that at a rate of application 5 kg/hectar the 50%-level of the initial amount of the insecticides was observed only by the end of the I2th week for the surface-applied chemicals and already by the 4th week for the soil-incorporated ones. No substantial differences in the content of soil-incorporated bazudin and dursban were ob-

Table 5. Dynamics of bazudin and dursban in three types of soil depending on the method of insecticide application (the rate of insecticide application 5 kg/hectare)

Insecticide	Method of application	Time after treatment, weeks	Insecticide content in soils,% of the initial amount		
			Soddy podzolic soil	Gray forest soil	Cher-nozem
Bazudin	Surface-applied	I	95	95	98
		2	87	9I	93
		4	82	89	88
		8	60	58	62
		I2	42	4I	42
		I6	32	39	36
	Soil-incorporated	I	88	90	90
		2	78	6I	63
		4	58	50	40
		8	38	25	30
		I2	25	I8	I7
		I6	20	7	II
Dursban	Surface-applied	I	89	94	94
		2	88	86	84
		4	85	78	78
		8	63	67	62
		I2	54	56	52
		I6	4I	43	48
	Soil-incorporated	I	88	90	93
		2	80	78	65
		4	63	49	4I
		8	47	40	32
		I2	48	27	2I
		I6	34	8	II

served in the first four weeks after the application,though later on bazudin decomposed more rapidly than dursban. For surface-applied granulated bazudin and dursban we observed the following: at first bazudin decomposed more slowly, then the reverse process occurred, and by the 8th week the content of dursban in the soil was higher than that of bazudin. It should be emphasized that both insecticides decomposed more rapidly in gray forest and chernozemic soils.

The influence of the soil type on the dynamics of insecticides at various rates of their application is shown in Table 6. The data presented indicate that in the soddy podzolic and chernozemic soils dursban decomposes much more slowly than bazudin, which permits to reduce their application rates to control pests.

Table 6. Dynamics of the in-row applied bazudin and dursban in soils, depending on their application rates

Soil type	Time after application, weeks	Insecticide content in soils (% of the initial amount)			
		Rate of bazudin application, kg/hectare		Rate of dursban application, kg/hectare	
		I.25	3.0	0.75	I.25
Soddy podzolic soil	4	60.0	54.5	63.4	68.2
	8	32.7	36.9	36.5	49.2
	I2	I7.3	23.I	34.I	38.5
	I6	I4.0	I7.0	16.1	33.3
	24	I0.5	I0.7	3.9	30.I
Chernozem	4	29.7	42.5	37.7	53.7
	8	I2.I	29.3	I5.5	35.8
	I2	I0.0	I6.I	9.I	26.8
	I6	5.5	I2.5	3.8	23.8
	24	5.I	7.7	2.7	I9.4

Studies on pesticide migration through the soil profile indicate that there is only slight movement of these pesticides both in vertical and horizontal directions. The character of pesticide distribution in horizons is determined primarily by water solubility of a chemical.

The results of our studies suggest that an investigation of the problems of pesticide translocation and transformation in the environment, soil included, should be correlated with a thorough research into the effects exerted on the processes of pesticide migration not only by physical-chemical and biological factors but also by those factors which are associated with the agricultural and economic activity of man. It is necessary to carry out zonal observations on the behavior of pesticides introduced to agrocenoses, taking into account agricultural and climatic features of regions, thus making possible to create the necessary prerequisites for a reliable ecological prediction of the behavior of xenobiotics in soils and other objects.

When monitoring environmental pollution, one should consider that most pesticides are only slightly stable in the environment and decompose there during one vegetation period. Therefore, a more correct approach to predicting a long-term residence of toxic substances in natural environments is required. Special emphasis should be given to the products of pesticide transformation which can be rather resistant to the influence of environmental factors and have unwanted remote effects on man, useful fauna and flora. Studies in this area are currently being carried out by a limited number of scientists, and therefore we consider it extremely important to direct efforts to more intensive study of this problem. First of all it is necessary to work out unified methodical principles and provide researchers with instruments of high sensitivity and adequate selectivity. The studies based on the unified methodical principles will make it possible to assess more objectively the results obtained by researchers from various countries participating in solution of the problem of protecting man and its environment.

SOIL PROCESSES AND THEIR USE IN PREDICTING VOLATILIZATION OF PESTICIDES FROM SOIL

by

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ABSTRACT

Volatilization of pesticides is a major pathway for their dissipation from soil. In addition, transport in the atmosphere is probably the principal mechanism for the wide dispersal of pesticides in the environment far from the site of application. Large quantities of pesticides eventually reach the soil either by direct application, wash-off from treated plant surfaces, redeposition from volatilized material or by land-disposal of pesticide waste. Significant progress has been made in our ability to predict pesticide volatilization from soil. This paper will discuss some of the soil processes influencing volatilization and their use in predictive models. The volatilization of surface-applied pesticides will depend on its vapor pressure as influenced by adsorption on soil surfaces and on its rate of removal from the soil surface by transport into the atmosphere. The rate of volatilization of soil-incorporated pesticides will depend not only on its vapor pressure and rate of removal from the soil surface by transport into the atmosphere but also on its rate of movement to the soil surface either by diffusion or by a combination of diffusion and convection in water moving to the soil surface. The quantities of pesticide available for transfer to the soil surface and therefore available for volatilization will depend on the distribution of the organic chemical between the soil, water, and air phases of the soil. A chemical distributing itself primarily into the vapor phase will move by vapor phase diffusion and its movement will depend in part on those soil factors control-ing vapor phase diffusion. A chemical distributed into the soil solution will move by convection and its movement will be dependent on water flow characteristics of the soil. The distribution of a chemical into the various phases will depend on the physical-chemical properties of the pesticide and of the soil. The primary physical-chemical properties needed to predict volatilization from soil are reliable vapor pressure and solubility data for the chemical and its partitioning coefficient between solid and aqueous phases of the soil. The partitioning coefficient will be determined by such soil factors as soil organic matter and clay contents. Henrey's constant, which describes the distribution of a chemical between vapor and solution, has been shown to be valid for soil systems. Several laboratory-based studies have been used to validate mathematical models for predicting pesticide volatilization from soil. Predictions from laboratory-based models would be expected to be useful for many purposes.

INTRODUCTION

Volatilization has been recognized as one of the major pathways by which pesticides are dissipated into the environment following their application or disposal. Several excellent reviews are available on various aspects of the volatilization process (1, 2, 3, 4, 5, 6, 7). Volatilization may take place from the spray droplets before they arrive at the target area and be carried away along with some of the spray droplets as part of what is referred to as drift. This paper will not deal further with the subject of drift. Volatilization may also take place from the surface of the treated area such as from plant and soil surfaces. Spencer, Farmer and Cliath (2) have reviewed the various processes and factors influencing the rate of volatilization from plant and soil surfaces. This paper will treat primarily the volatilization of pesticides from soils. Many of the principles involved will apply to volatilization of other compounds and to volatilization from other surfaces.

Volatilization from soils can be described as a three-step process. All steps in the process will not be necessary under all conditions. The pesticide compound must move to the soil surface. This step applies particularly to the volatilization of soil-incorporated pesticides and in many cases will be the process controlling the rate of volatilization. For pesticides that are only surface-applied, this step in the volatilization process will not be significant unless the pesticide is subsequently leached into the soil by rain or irrigation waters. Movement to the soil surface can take place by diffusion of the pesticide molecules in either the vapor phase or in the non-vapor phase, movement to the soil surface by convection when water is evaporating from the soil surface, or, as is often the case, by a combination of convection and diffusion processes. Often, when convection is operating to bring pesticides near the soil surface and the pesticide is evaporating from the soil surface as rapid as it is transported there, essentially zero pesticide concentration at the soil surface is maintained. This results in a high pesticide concentration gradient near the surface. Under these conditions, diffusion will control the movement of pesticide in the last several millimeters of soil near the surface while convection is bringing up additional pesticide from deeper in the soil. Hartley (8) has used the term "wick effect" to describe the influence of evaporating water on moving pesticides to the soil surface and thereby enhancing the volatilization rate of pesticides. Several reviews are available covering transport of pesticides in soils (9, 10, 11, 12).

A second step in the volatilization process is the transfer of the pesticide to the vapor phase. This step can take place either within the soil profile or at the soil surface. When movement to the soil surface is by vapor phase diffusion, the transfer to the vapor phase will take place within the soil profile before the movement step can occur. The transfer of pesticide to the vapor phase is controlled by all those factors of the soil, the pesticide, and the environment which control the distribution of a compound between the soil, water, and air phases. This step is a particularly important process, since it controls the vapor density or the vapor concentration of the pesticide.

The third step in the volatilization process will be the movement of the pesticide away from the soil surface either by diffusion into the atmosphere or by turbulent mixing with the air above the soil.

The extent to which these three steps interact under actual field conditions to control volatilization can be highly complex depending on the soil, the particular pesticide, and the environmental conditions. For example, for a pesticide that is mobile in the aqueous phase alternate wetting and drying periods in the soil may have the pesticide first moving down into the soil profile with infiltrating water before moving back toward the soil surface. For most of these field conditions, the factors which influence the distribution of pesticides between the soil, water, and air phases are well-known. The partitioning between the various phases can be predicted from a few basic properties of the pesticide and of the soil. The factors involved and how they are used to predict partitioning into the soil, water, and air phases will be presented in this paper. Our ability to predict the movement to the soil surface under field conditions is limited because of the large variabilities in soil properties encountered in the field. However, from a consideration of laboratory-based transport models under well-defined conditions, useful information can be determined on the relative volatilization rate of different pesticides. In this paper, some of the laboratory-based models for predicting pesticide volatilization will be examined to determine those parameters important in controlling volatilization.

PESTICIDE PARTITIONING BETWEEN SOIL, WATER AND AIR

The extent to which a pesticide partitions itself between the solid, liquid, and gaseous phases of the soil will determine the amount of pesticide available in the soil solution and in the air pores of the soil for transport to the soil surface as well as the amount of pesticide in the air phase at the soil surface for loss to the atmosphere as volatilized pesticide.

The total soil pesticide concentration, C_T (μg cm^{-3} soil) and the pesticide concentration in the three soil phases are given by

$$C_T = \rho_b S + \theta C_l + P_a C_g \qquad [1]$$

where S is the adsorbed concentration (μg g^{-1} soil), C_l is the liquid concentration (μg cm^{-3} solution), C_g is the gas concentration (μg cm^{-3} air), ρ_b is soil bulk density (g cm^{-3}), θ is volumetric water content (cm^3 cm^{-3}) and P_a is air-filled porosity (cm^3 cm^{-3}).

A pesticide will distribute itself between the vapor, liquid and adsorbed phases of Eq. [1] according to the following relationships:

1) Adsorption of a pesticide from the solution phase onto the solid phase can be described by either the linear adsorption isotherm

$$S = K_d C_l + \beta \qquad [2]$$

or the Freundlich isotherm

$$S = k\, C_l^{N} \qquad [3]$$

where K_d, β, k, and N are empirically derived constants, with β often assumed to be zero. Eq. [2] is often used in model development because of its simplicity. The error involved when N is different than one can be minimized by evaluating K_d and β over a narrow concentration range.

2) The distribution of a pesticide between the gas and liquid phases is given by Henry's Law:

$$C_g = K_H C_l \qquad [4]$$

where K_H (cm^3 air cm^{-3} liquid) is referred to as Henry's Law Constant.

Spencer and Cliath (13) have confirmed the applicability of Henry's Law to soil-pesticide systems. Figure 1, taken from Spencer and Cliath (13), is a comparison of the vapor phase desorption of a volatile compound, in this case lindane, from a silt loam soil with the solution phase

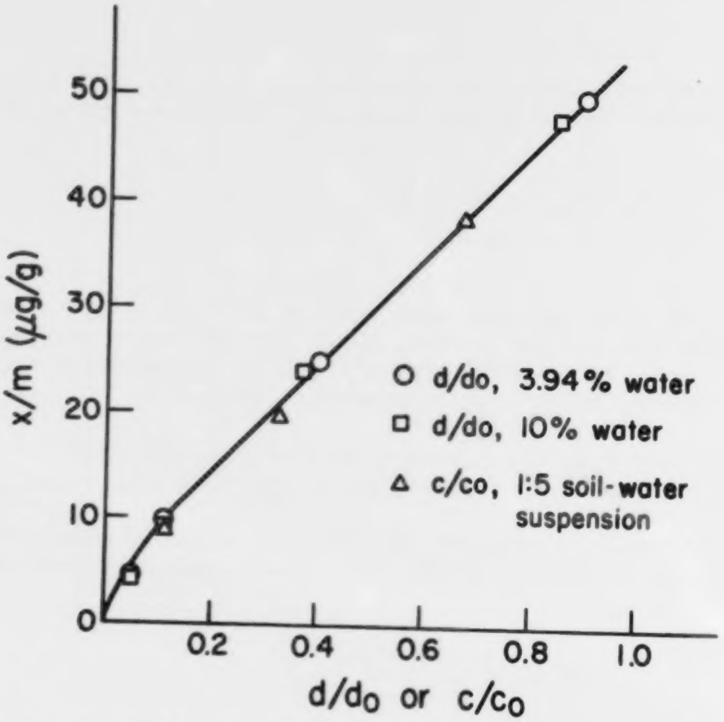

Figure 1. Desorption isotherm for lindane in Gila silt loam at 30C relating adsorbed lindane (x/m) to relative vapor density (d/d_o) and to relative solution concentration (c/c_o). From Spencer et al. (19).

desorption of lindane from the same silt loam soil. In Figure 1, x/m is the adsorbed concentration, d is the gas concentration, and c is the liquid concentration equivalent to S, C_g, and C_l, respectively, in this paper, and the subscript o refers to the saturation vapor density or maximum solubility of the pure compound without soil. The data for the vapor phase desorption and solution phase desorption are both seen to fall on the same line. This means that the amount of adsorbed pesticide required to give a saturated vapor density in a soil suspension is the same as the amount required to give a saturated solution and for any degree of saturation.

The use of the relationships expressed in Equations [2], [3] and [4] in conjunction with Equation [1] allows one to express C_T in terms of a single phase, e.g., C_g, an essential step in any predictive efforts. This paper will not present the mathematical details of modeling the volatilization of pesticides as the details have been presented by others in publications to be discussed in later sections. However, a review of some of the more important factors that influence the values of the coefficients K_d, k, and K_H of Equations [2], [3] and [4] will be presented. Those factors of particular utility in predicting pesticide volatilization are temperature, pesticide concentrations, soil water content, and soil organic matter content.

As has already been seen, soil pesticide concentration expresses its effect on volatilization through the coefficients in Equations [2] - [4]. Generally, the higher the total concentration, the higher will be the concentration in any of the soil phases. Several soil properties will influence the distribution among the various phases including soil organic matter, clay content, and soil pH (14, 15, 16). Of these properties, soil organic matter has been shown to be the most important property in determining the value of the distribution coefficients for non-ionic and weakly polar compounds. Pesticides which are non-ionic and weakly polar compounds are also the ones which tend to be volatile. As soil organic matter increases, the pesticide is more strongly adsorbed in the solid phase leading to less chemical in both the liquid and solid phases. For the solution phase, this phenomena has been well documented in the literature. For the gas phase, dieldrin vapor pressure in five soils was found to vary inversely with soil organic matter content (17). The effect of soil organic matter on the distribution coefficient can be expressed through the relationship

$$K_{OC} = (K_d/\text{percent organic carbon})100 \qquad [5]$$

Hamaker (1) used this relationship to estimate the relative vapor behavior of pesticides in soils from vapor pressure, water solubility and K_{OC} values.

The effect of temperature on pesticide volatilization is primarily through its effect on vapor pressure. The effect of temperature on the aqueous phase distribution (e.g., K_d) and on the diffusion coefficient are both slight compared to the effect on the vapor pressure. Increasing temperature increases both the pesticide aqueous solubility and the vapor pressure. However, the effect on vapor pressure is greater than that on solubility so that increasing temperature increases the value of K_H resulting in an increased vapor concentration.

The effect of soil water content on pesticide vapor density and on volatilization is especially interesting. The influence of water can best be considered along with effects due to pesticide concentration. At soil water contents less than that equivalent to a monolayer of water molecules covering the soil surface, relatively non-polar compounds are strongly adsorbed by soil surfaces yielding greatly reduced vapor pressures and very low K_H values. This effect is evident even at relatively high soil pesticide concentrations. Whereas in a moist silt loam soil, dieldrin (18), lindane (19), p,p'-DDT (20), o,p'-DDT (20), and trifluralin (21) reached their maximum vapor pressure at soil concentrations of 25, 55, 15, 39, and 73 $\mu g\ g^{-1}$, respectively, these same concentrations will yield essentially zero or extremely low-vapor pressures in the same soil when dry. In a moist soil, water molecules successfully compete with pesticide molecules for adsorption sites leading to a higher vapor pressure and therefore higher volatilization of pesticides from a moist compared to a dry soil.

MODELS PREDICTING VOLATILIZATION FROM SOIL

Typical volatilization flux curves for the volatilization of soil-incorporated pesticides exhibit an initial high flux rate followed by a rapidly decreasing rate as surface pesticide concentrations are depleted (22, 23, 24). At this point the rate of volatilization will be dependent on the rate of movement of the chemical to the soil surface. Movement to the soil surface will be by diffusion or by a combination of diffusion and convection with evaporating water. The actual movement will be determined by all of the factors controlling the partitioning of the pesticide between the soil, liquid and gas phases. The models discussed in this paper will generally assume that transport to the soil surface is the rate-limiting step.

Most mathematical models for predicting volatilization from soil that have been tested have used data derived from well-controlled laboratory experiments. Field validation of volatilization models will necessarily be slow because of difficulties in accounting for all experimental variables. However, the current laboratory-based models will be useful for providing information on relative volatility rates based on properties of the pesticide and of the soil.

Diffusion Models

A number of models have been developed predicting volatilization of soil-incorporated pesticides for the case when diffusion to the soil surface is controlling movement (1, 25, 26, 27, 28). These models are applicable in the absence of mass flow of the pesticide to the soil surface. Mass flow would not be operating when there is no net-evaporation of water from the soil surface or in the case of compounds, such as pesticides with extremely low water solubilities, which distribute in the solid, liquid and gas phases in such a way as to present little pesticide in the soil solution for movement with evaporating water.

Mayer, Letey and Farmer (26) and Farmer and Letey (25) have presented several models to predict the volatilization of soil-incorporated pesticides when diffusion was the principle means of pesticide transport to the soil surface. The choice of models varies depending on the depth of treated soil and on air speed moving over the soil surface. One of the models assumes a non-moving air layer of various depths above the soil surface so that the pesticide concentration gradient in the air controls the rate of volatilization. For the models where concentration at the soil surface is assumed to be zero, and transport to the soil surface is therefore controlling volatilization, the volatilization flux would be dependent on the initial concentration, the depth of the treated soil layer, and on the apparent diffusion coefficient of the pesticide in soil. Care must be taken in applying any model that utilizes the diffusion coefficient of a pesticide through soil. The value of the apparent diffusion coefficient depends on various parameters including bulk density, water content, concentration, temperature and adsorption (29). Good agreement was found by Mayer et al. (26) between predicted and experimental values for the volatilization of lindane and dieldrin from a silt loam soil. Figure 2 shows the agreement between Model II of Mayer et al. (26) and data taken from Spencer and Cliath (23) for the volatilization of dieldrin from soil in a laboratory study. The predicted values (solid curve) in Figure 2 were calculated from

$$J_p = DC_T/(\pi D\ t)^{1/2} \qquad [6]$$

where J_p is the pesticide flux, D is the apparent diffusion coefficient for pesticide diffusion in soil and t is time. The equation assumes that the depth of the treated layer is sufficiently deep that it does not influence the volatilization flux in time, t, and that the pesticide volatilizes and is removed rapidly maintaining a zero concentration at the

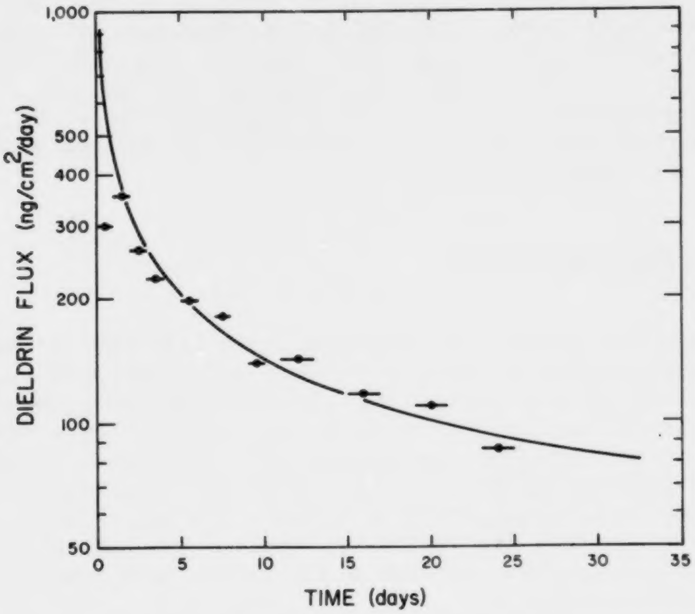

Figure 2. Predicted (solid curve) and measured volatilization flux from a soil surface for a diffusion experiment. Predicted values derived from Model II of Mayer et al. (26). The experimental values taken from Spencer and Cliath (23). The length of the horizontal lines indicate the length over which the experimental values were taken. From Mayer et al. (26).

soil surface. The diffusion coefficient for dieldrin was taken from Igue et al. (30). The good agreement between measured and calculated values indicates that under these conditions zero concentration at the soil surface was a reasonable assumption.

Volatile compounds buried in soil such as pesticide wastes or other industrial organic wastes placed in landfills present a special circumstance for volatilization because of the large concentration gradients that are created across the soil layer covering the wastes. Farmer et al. (27, 28, 31) developed and tested a model for predicting vapor loss of hexachlorobenzene (HCB) from a landfill covered with soil. The model is based on vapor-phase diffusion through the air-filled soil pores and would be applicable to predicting steady-state volatilization of other chemicals which move primarily in the vapor phase. The equation derived to predict steady state vapor loss is based upon the vapor diffusion coefficient in air, D_o.

$$J_p = D_o P_a^{10/3}(C_2-C_S)P_T^2 L \quad [7]$$

where C_2 is the vapor concentration at the soil surface, C_S is vapor concentration at the bottom of the soil layer, P_T is the total soil porosity and L is the soil depth. The validity of Equation [7] was experimentally varified with HCB using a simulated landfill apparatus in the laboratory (27, 28, 31). It can be seen from Equation [7] that under these conditions, volatilization flux will be strongly influenced by the soil air-filled porosity which in turn is determined by soil water content and the degree of soil compaction (31).

Convection-Diffusion Models

Spencer and Cliath (23) have shown the influence of evaporating water on moving pesticides to the soil surface and thereby enhancing the volatilization rate of pesticides. In addition, they reported that the enhanced volatilization due to water loss was effective only after the surface soil pesticide concentrations were depleted. In the experimental studies of Spencer and Cliath (23), water was supplied to the bottom of soil columns to maintain moist soil while the relative humidity of the air passing over the soil was varied to regulate the rate of water evaporation from the soil. In their studies the flux due to convection was estimated from the relationship

$$J_p = J_w C_1 \quad [8]$$

where J_w is the water flux.

The concentration of the chemical in the soil solution was estimated from the distribution coefficient, K_d. With lindane, the flux calculated due to convection ranged from 356 to 703 μg cm^{-2} day^{-1} equivalent to 18-71% of the total lindane flux. Dieldrin flux due to convection ranged from 9.9 to 23.6 μg cm^{-2} day^{-1} equivalent to 3-33% of the total dieldrin flux. The increased contribution of convection to the volatilization flux of lindane compared to dieldrin was attributed to the lower K_d for lindane resulting in a higher solution concentration for movement to the soil surface.

An interesting finding in the study by Spencer and Cliath (23) was the accumulation of dieldrin at the dry soil surface when low relative humidity air was passed over the soil surface. When this soil was rewet by exposure to air flow at high relative humidity, the dieldrin volatilized at a high rate. In the field this would result in short term fluctuations in the volatilization rate as surface drying causes the pesticide to accumulate at the soil surface thereby reducing volatilization; however, upon rewetting the pesticide will volatilize so that over longer time periods volatilization should be directly related to water evaporation if the pesticide is moving to the soil surface in the evaporating water.

Jury et al. (24) have presented both a diffusion model and a combined diffusion-mass flow model for predicting volatilization of soil-incorporated pesticides. Their models, for a uniformly treated soil, assumes Henry's law applies to the gas and liquid concentrations, assumes a linear adsorption isotherm and that movement away from the soil surface was sufficiently rapid to maintain zero pesticide vapor concentration at the surface. To test the models, vapor losses of the herbicide triallate, which had been incorporated into two soils with widely different organic matter contents, were measured in the absence and presence of evaporating water. The results are shown in Figure 3. The solid line is predicted flux using the model for diffusion controlled volatilization (100 percent relative humidity). Good agreement as observed was expected between predicted and measured fluxes from the diffusion experiments because the apparent diffusion coefficients for triallate were evaluated from the experimental cumulative loss measurements. After nine days into the experiment water evaporation from the soil columns was induced by switching some of the columns to 50 percent relative humidity. In the case of the San Joaquin sandy loam, the soil with the lower soil organic matter content and lower K_d for triallate adsorption, the volatilization flux is seen to remain steady after nine days. In this soil convection is operating to move more pesticide to the soil surface to replace that lost by volatilization. For the Flanagan silt loam, which had the higher organic matter content and higher K_d value, there was not enough triallate in the solution phase to move significant amounts to the soil surface with evaporating water and the flux continues to decrease after nine days even when convection is operating. The predicted values (dashed curve) for the diffusion-convection experiments provide an upper limit for volatilization. In the case of the San Joaquin soil, the measured triallate flux approaches the predicted flux after 30 days. In the case of the Flanagan soil, the model tends to overestimate the contribution due to convection as the measured triallate volatilization flux remained close to that for pure diffusion. However, the combined diffusion-convection model did predict a greater influence of convection for the San Joaquin soil than for the Flanagan soil, as was observed.

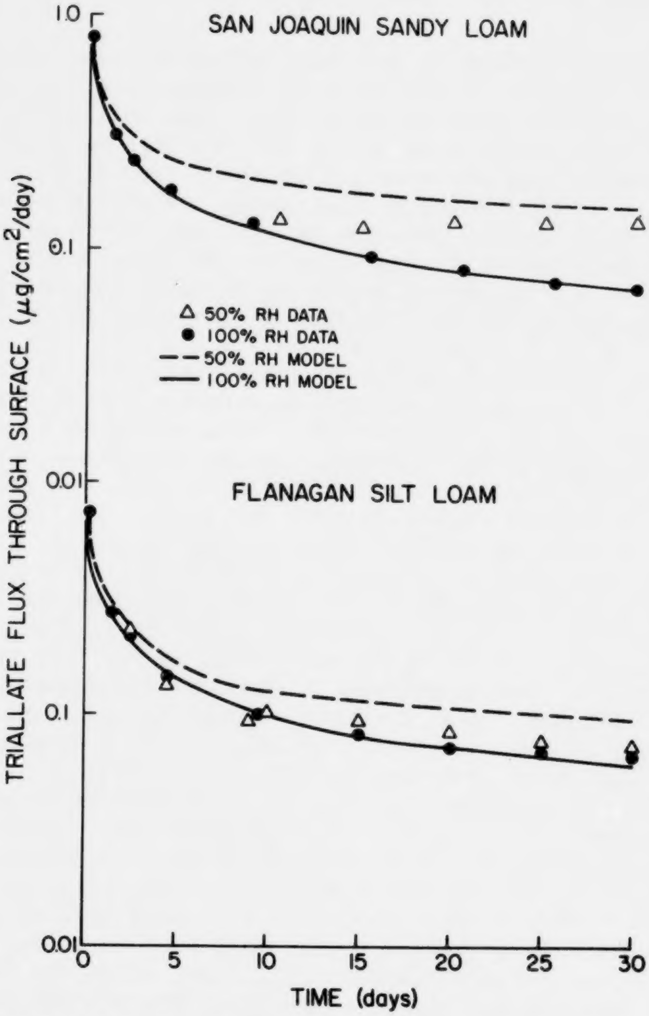

Figure 3. Predicted and measured volatilization flux from the surface of two soils for soil-incorporated triallate for the diffusion experiment (relative humidity = 100 percent) and the diffusion-convection experiment (relative humidity = 50 percent). The San Joaquin soil had a soil organic matter content of 1.24 percent and the Flanagan 5.5 percent. From Jury et al. (24).

DISCUSSION

The minimum information required to predict relative volatilization of a pesticide from soil would be vapor pressure and solubility of the pesticide at various temperatures and adsorption coefficients for the pesticide between the soil and solution phases. When this information is available for pesticides, predictive models such as those of Jury et al. (24) can be used to compare the potential for the different pesticides to volatilize from a soil with a known or assumed bulk density, water content and porosity. Diffusion coefficients in air and in water can be estimated if measured values are not available.

Other factors not considered here such as degradation rates, wind speed, surface roughness, and ground cover will also influence actual volatilization rates. The degradation rate of a pesticide will be a major factor in determining if volatilization would be a major pathway for dissipation of the pesticide. If a compound is highly volatile but is rapidly decomposed under certain environmental conditions, volatilization may not be a significant mode of loss under those conditions. On the other hand, if a compound is resistant to degradation, volatility losses can be significant even for a compound of low vapor pressure. A greater effort is needed to include degradation parameters in transport models.

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MODELING TRANSPORT AND DEGRADATION OF PESTICIDES IN THE SOIL AND SURFACE WATER ENVIRONMENTS

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ABSTRACT

This paper describes three mathematical models, HSPF, CREAMS and EXAMS, recently developed in the USA for simulating the behavior of pesticides and other chemicals in the soil and/or surface water environments. They are of the "deterministic conceptual" type. That is, they consist of sets of linked equations, each of which represents our understanding of some aspect of the problem. The equations include parameters which are, as far as possible, physically based. These models do not include random components.

The HSPF and CREAMS models simulate dynamic behavior. To achieve this the user supplies several different types of data, such as:

1. Continuous time series of input data such as precipitation, air temperature and solar radiation.

2. Information on intermittent activities such as soil tillage and chemical applications.

3. Many parameters, which make the model equations applicable to the site under study.

The models then operate on this information, evaluating the equations repeatedly, to simulate processes. The result is a set of outputs, such as simulated soil moisture, streamflow, and pesticide and nutrient concentrations.

The EXAMS model is different; it is designed to simulate the steady state situation in a set of water-bodies with steady chemical loading. It does, however, simulate the unsteady recovery period after chemical loading has terminated.

All the models start by estimating the movement of water and sediment (because these are the principal mechanism of chemical transport). The modeling of chemical reactions and degradation is then superimposed on this framework.

A central concept in the HSPF model is the separation of the "land" and "surface water" phases of the hydrological cycle. To model pesticides in the land phase, HSPF includes the processes of advection, adsorption/desorption, degradation and volatilization. CREAMS is similar, in this respect, but EXAMS does not model the land phase.

The processes which HSPF considers for modeling organic compounds in the surface water phase are:

1. Adsorption/desorption on six classes of sediment, namely sand, silt and clay both in suspension and in the bed.

2. Deposition and scour of sediment-attached material.

3. Advection of dissolved and adsorbed material.

4. Degradation, from the dissolved state, through hydrolysis, photolysis, volatilization, biodegradation and oxidation by free radicals.

5. The formation of "daughter" compounds through the degradation of "parent" compounds.

The EXAMS model considers a similar range of processes, while the CREAMS model does not include the surface water phase.

This paper also discusses some features of modern model construction, such as:

1. The use of Structured Programming Technology. This permits a model to have a clear hierarchical structure, with

each subroutine performing a well-defined task. The resulting ease of program maintenance and alteration or addition is discussed.

2. The concept of subdividing a study area into a set of "processing units." This idea, present both in HSPF and EXAMS, provides the user with great flexibility in applying the model to complex networks of land and surface water units.

3. The use of sophisticated input scanners which check user-supplied values for reasonableness, insert default values where necessary and interpret time series linkage instructions.

INTRODUCTION

In this paper we discuss three mathematical models which simulate the behavior of pesticides (and other water quality constituents) in the land and stream phases of the hydrological cycle:

1. The Hydrologic Simulation Program - Fortran (HSPF), developed under sponsorship of the United States Environmental Protection Agency (U.S. EPA).

2. Chemicals, Runoff and Erosion from Agricultural Management Systems, developed by scientists in the United States Department of Agriculture (USDA).

3. The EXposure Analysis Modeling System (EXAMS), developed by the U.S. EPA.

For the sake of brevity we will refer to them, simply, as HSPF, CREAMS and EXAMS. These computer programs have all been developed recently and are representative of the wide variety of models now being used in the USA for water quality studies. The three models are all "deterministic conceptual;" that is, they consist of linked mathematical relationships which approximate the actual processes occurring in nature, and they have no built-in random components.

We will first discuss HSPF in some detail, then we will briefly discuss CREAMS and EXAMS and compare them with HSPF. There are two reasons for this approach:

1. HSPF simulates processes occurring both in the soil profile and in streams (Figure 1); the other models consider only a subset of these processes.

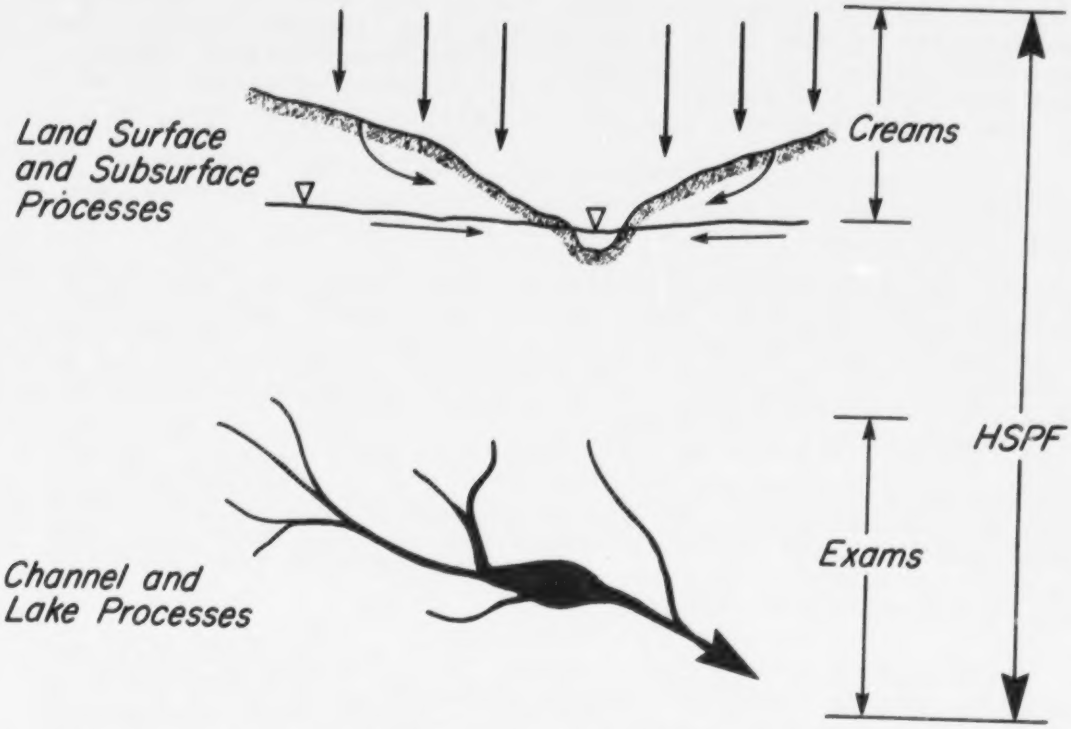

Land Surface and Subsurface Processes
Creams
HSPF
Channel and Lake Processes
Exams

Figure 1. Portions of the Hydrological Cycle Covered by the Models Discussed

2. We have been deeply involved in the development of HSPF but are not as familiar with the other models.

We will start with a brief overview of the entire HSPF system and then concentrate on those parts that are especially relevant to pesticide simulation.

OVERVIEW OF THE HSPF MODEL

HSPF was developed from a set of earlier models, the most important of which were:

1. The Stanford Watershed Model (SWM) developed at Stanford University (Crawford and Linsley 1966). It can simulate the hydrologic behavior of an entire watershed.

2. The Agricultural Runoff Management (ARM) Model, developed by Hydrocomp Inc. for the U.S.EPA (Donigian et al 1977). It

simulates the hydrology, sediment yield, and nutrient and pesticide behavior of the land phase of the hydrological cycle. The same organizations also developed the Non-Point Source (NPS) Model (Donigian & Crawford 1976) which handles the washoff of user specified, sediment correlated pollutants from the land.

3. The HSP Quality Model (Hydrocomp 1977). It simulates a comprehensive set of water quality processes in streams and lakes, but not pesticides and toxic substances.

4. The SERATRA Model, developed by Batelle Northwest Laboratories (Onishi and Wise 1979). This model was designed to simulate the behavior of sediment and associated constituents in streams. It includes processes such as hydrolysis and photolysis and is, thus, suitable for modeling pesticides.

When work started on HSPF in 1976 the objective was to merge most capabilities of the above models into a single set of software, with a unified structure and written in the standard Fortran IV language (A.N.S.I 1966). The approach taken involved the following:

1. A completely new design. Rather than "patching" parts of the older models together, their functions were fitted into a totally new software framework. The concepts of Structured Programming Technology (IBM 1974) were applied to this design. The entire set of software was arranged in hierarchical order, shown on a structure chart. The general idea was that the entire system should form a tree, branching out from the MAIN sub-program (Figure 2). "Continuation flags" point to subordinate structure charts, so that the entire HSPF program can be viewed by studying the 80 structure charts needed to completely describe it. Within each sub-program, instructions were first coded in "pseudo code," similar to Algol (Figure 3). In accordance with the tenets of structured programming, as developed by Dijkstra and others during the 1960's, the pseudo code included only the following five basic "structure figures:" SEQUENCE, IF-THEN-ELSE, DO-UNTIL, WHILE-DO and CASE. The pseudo code was then translated to standard Fortran. The benefits of writing in structured code, compared to Fortran, should be readily apparent from Figure 3.

2. The breakdown of a catchment into "processing units." A fundamental concept in the models from which HSPF was developed was that the land surface and subsurface processes could be separated from processes in stream channels. Furthermore, the various land surfaces in the catchment could be subdivided into quasi-homogeneous "land-segments," and the channel system into a set of "reaches" (Figure 4). This view of the world was preserved in HSPF. Each processing unit

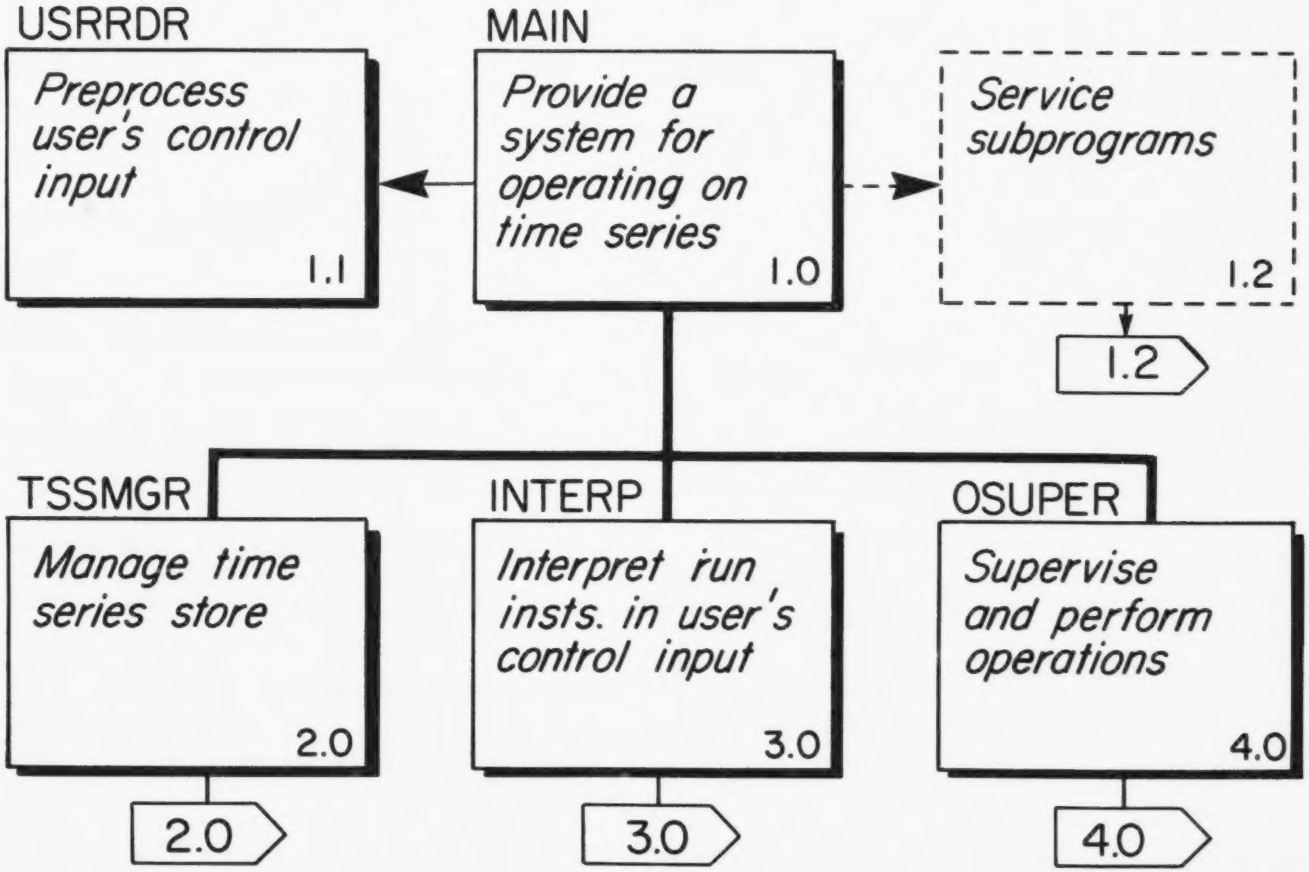

USRRDR
Preprocess user's control input
1.1
MAIN
Provide a system for operating on time series
1.0
Service subprograms
1.2
1.2
TSSMGR
Manage time series store
2.0
2.0
INTERP
Interpret run insts. in user's control input
3.0
3.0
OSUPER
Supervise and perform operations
4.0
4.0

Figure 2. Structure Chart of the Upper Levels of HSPF Software

PSUEDO CODE:

```
4.2(14).1

BEGIN DURDMP (J1,J2,LGTH,FREQ,S,SQ,K,NDUR,
             DURAT (*))

INTEGER*2 I,J,J1,J2,NDUR,DURAT (10)
INTEGER*4 K,LGTH (22)
REAL      FREQ(10,K),S(10,K),SQ(10,K)

  J= J1
  WHILEDO J <= J2
    I = 1
    WHILEDO DURAT (I) <LGTH(J) and I < = NDUR
      FREQ(I,J)= FREQ(I,J)+1
      S(I,J)= S(I,J) + LGTH (J)
      SQ(I,J) = SQ(I,J) + LGTH (J)*LGTH (J)
      I= I + 1
    ENDDO

    LGTH (J) =  0
    J= J+ 1
  ENDDO

END DURDMP
```

FORTRAN WITH NO INDENTATION OF STATEMENTS:

```
C   4.2(14).1
C
    SUBROUTINE DURDMP (J1,J2,LGTH,FREQ,S,SQ,K,NDUR,DURAT)

C
C   + + DUMMY ARGUMENTS + +
    INTEGER*2 J1,J2,NDUR,DURAT (10)
    INTEGER*4 K,LGTH (22)
    REAL      FREQ(10,K),S(10,K),SQ(10,K)
C
C   + + LOCAL VARIABLES + +
    INTEGER*2 I,J
C
    J = J1
 10 IF (J.GT.J2) GO TO 40
    I= 1
 20 IF ((DURAT(I).GT.LGTH(J)).OR.(I.GT.NDUR)) GO TO 30
    FREQ (I,J)= FREQ(I,J) + 1
    S(I,J)= S(I,J)+ LGTH(J)
    SQ(I,J)= SQ(I,J)+ LGTH(J) *LGTH (J)
    I= I+ 1
    GO TO 20
 30 CONTINUE
    LGTH(J)= 0
    J= J+1
    GO TO 10
 40 CONTINUE
C
    RETURN
    END
```

Figure 3. Contrast Between "Pseudo Code," Used in HSPF, and Typical Fortran Programming

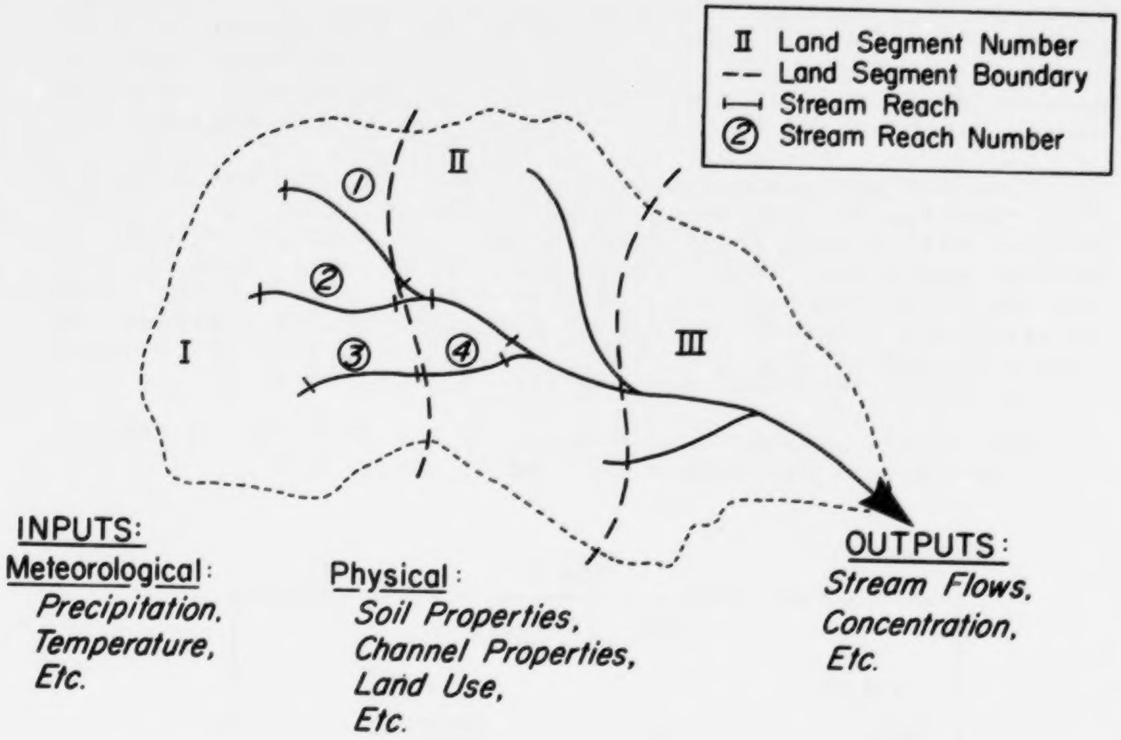

II Land Segment Number
-- Land Segment Boundary
Stream Reach
② Stream Reach Number
①
②
③
④
I
II
III
INPUTS:
Meteorological:
Precipitation,
Temperature,
Etc.
Physical:
Soil Properties,
Channel Properties,
Land Use,
Etc.
OUTPUTS:
Stream Flows,
Concentration,
Etc.

Figure 4. Breakdown of a Catchment into Land-Segments and Stream Reaches

(land segment or channel reach) is simulated independently of others, except for contributions from upstream units.

3. The use of continuous simulation. In HSPF, the user can choose a simulation interval ranging from 1 minute to a day. Once selected, this time step remains constant throughout the simulation.

The result of the HSPF development was a set of software consisting of:

1. Application and Utility Modules (Figure 5). Application modules simulate processes. They use input time series such as precipitation, air temperature and solar radiation, and produce output time series such as computed flows and constituent concentrations at various points in the catchment. The user must also supply values for parameters and initial conditions. At present, HSPF has a Pervious Land-segment (PERLND) Module, an Impervious Land-segment (IMPLND) Module and a (stream) Reach/Reservoir (RCHRES) Module. Utility modules do not simulate processes; they merely assist the user

by performing functions on time series, such as: copying, generating information for display on an incremental plotter or in a printed table, or the analysis of time series. Because HSPF is totally modular, it is relatively easy to modify existing modules or to add new ones to the system.

2. Time Series Management System (TSMS). This is the software that supplies an operating module (application or utility module) with needed input time series and passes output to another operation (e.g. flow and constituent data passed between river reaches) or to a disc storage medium - the Time Series Store. Figure 6 shows the interaction between an operating module and the TSMS, which consists of modules TSGET, TSPUT, the INPAD and the Time Series Store.

The entire system is documented in the HSPF User's Manual and Programmer's Supplement (Johanson, et al 1980).

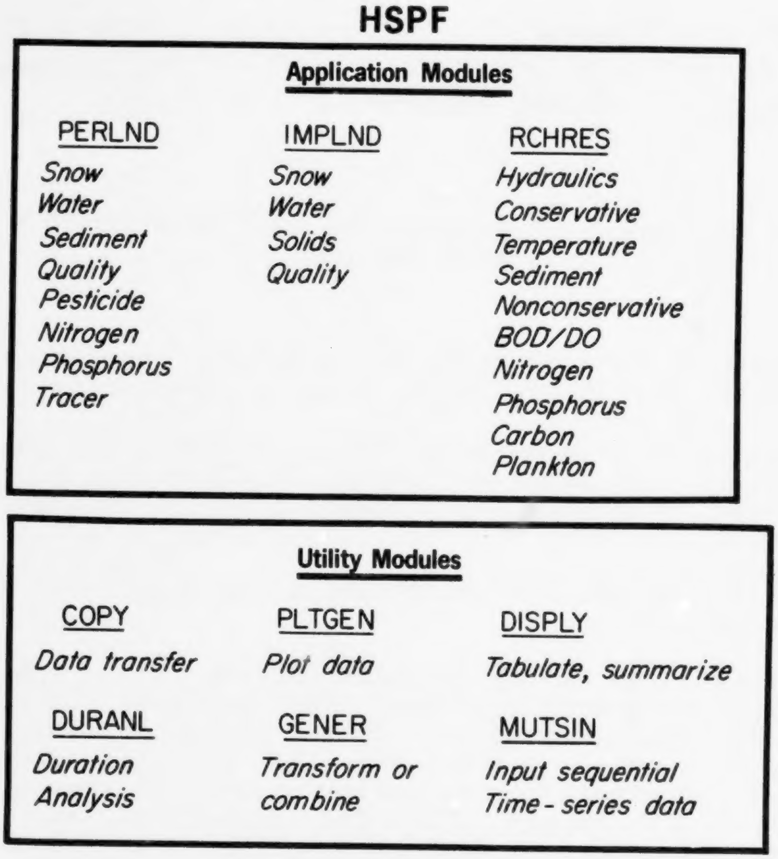

HSPF
Application Modules
PERLND
Snow
Water
Sediment
Quality
Pesticide
Nitrogen
Phosphorus
Tracer
IMPLND
Snow
Water
Solids
Quality
RCHRES
Hydraulics
Conservative
Temperature
Sediment
Nonconservative
BOD/DO
Nitrogen
Phosphorus
Carbon
Plankton
Utility Modules
COPY
Data transfer
PLTGEN
Plot data
DISPLY
Tabulate, summarize
DURANL
Duration Analysis
GENER
Transform or combine
MUTSIN
Input sequential Time-series data

Figure 5. "Operating Modules" Presently in the HSPF Software

THE HSPF PERVIOUS LAND-SEGMENT (PERLND) MODULE

General Comments

The PERLND module simulates a variety of processes occurring on and under the surface of a pervious land-segment. The structure chart (Figure 7) shows its various functions and the names of the twelve sections of the module which handle those functions. The sections usually involved in simulating pesticides are SNOW and PWATER (hydrology), SEDMNT (sediment), MSTLAY (solute transport) and PEST (pesticides). The last 5 sections of the module are of primary importance in simulating agricultural chemicals.

The user specifies which set of sections will be executed in a given run. For example, he may initially "switch on" only SNOW and PWATER, to calibrate the simulated hydrological behavior of a land-segment to observed data. Then he may turn on MSTLAY and TRACER so that he can compare the simulated and observed movement of a conservative substance such as chloride. Finally, he may turn TRACER off and PEST on, to simulate up to 3 pesticides.

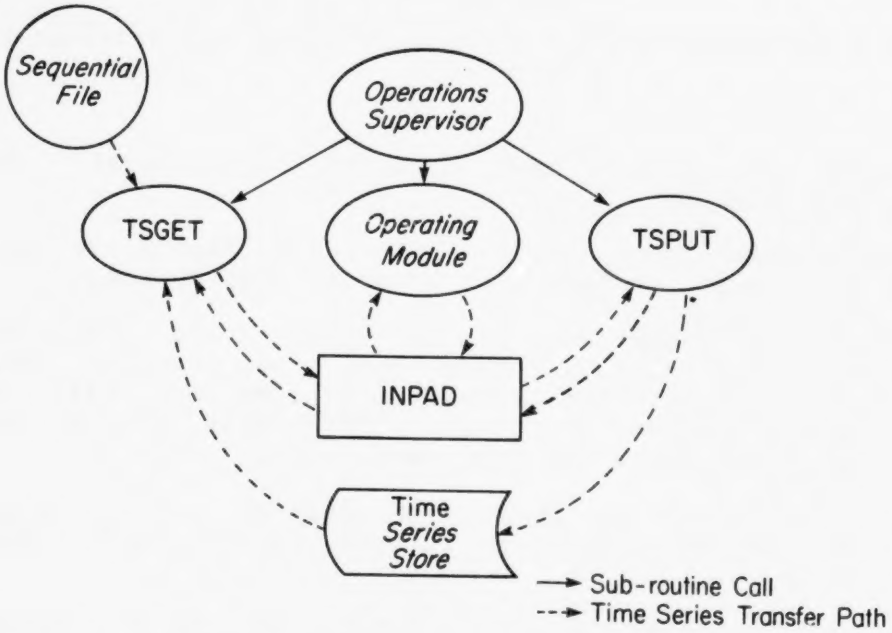

Sequential File
Operations Supervisor
TSGET
Operating Module
TSPUT
INPAD
Time Series Store
Sub-routine Call
Time Series Transfer Path

Figure 6. Activities Involved in Executing an HSPF Operation

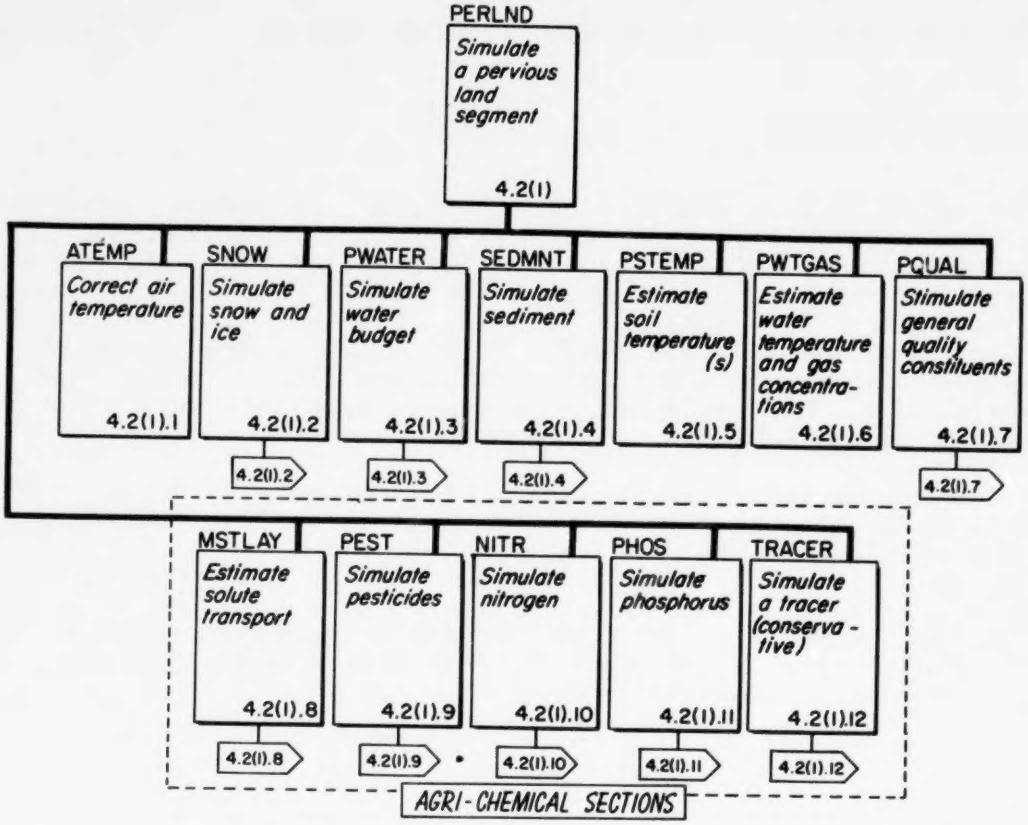

PERLND
Simulate a pervious land segment
4.2(1)
ATEMP
Correct air temperature
4.2(1).1
SNOW
Simulate snow and ice
4.2(1).2
PWATER
Simulate water budget
4.2(1).3
SEDMNT
Simulate sediment
4.2(1).4
PSTEMP
Estimate soil temperature (s)
4.2(1).5
PWTGAS
Estimate water temperature and gas concentrations
4.2(1).6
PQUAL
Stimulate general quality constituents
4.2(1).7
4.2(1).2
4.2(1).3
4.2(1).4
4.2(1).7
MSTLAY
Estimate solute transport
4.2(1).8
PEST
Simulate pesticides
4.2(1).9
NITR
Simulate nitrogen
4.2(1).10
PHOS
Simulate phosphorus
4.2(1).11
TRACER
Simulate a tracer (conservative)
4.2(1).12
4.2(1).8
4.2(1).9
4.2(1).10
4.2(1).11
4.2(1).12
AGRI-CHEMICAL SECTIONS

Figure 7. Structure Chart for the HSPF Pervious Land-segment Module

The HSPF system has been made as "intelligent" as possible. For example:

1. If a user omits some input, HSPF will supply default values if they exist, or report an error if they do not.

2. It will ignore unnecessary input. Thus, if a user has been simulating pesticides and then turns that section off, possibly to re-calibrate the hydrology, he does not have to delete the pesticide-related input. HSPF will ignore it, until he once again turns the PEST section on.

3. It can accept input in Metric or English units. (e.g. pesticide application in kg/ha or lb/acre, rainfall and runoff in mm or inches).

4. It can supply printed output in Metric or English units (or both), regardless of the units used for the input.

Furthermore, printed output can be supplied at several specified frequencies: N time steps, 1 day, 1 month, 1 year, or never.

5. Any one (or several) of many time series can be selected for special display, either on a plotter or in specially formatted printed tables.

The above points apply to all the application modules; not just the PERLND module.

Hydrologic Simulation in the PERLND Module

Hydrologic simulation is done using the moisture accounting technique first employed in the Stanford Watershed Model (Figure 8). That is, the movement of water into, between, and out of, a set of conceptual storages is computed using a fixed time step. Snow accumulation and melt are simulated in the SNOW section (if it is turned on) using energy balance procedures (U.S. Army Corps of Engineers 1956). Rain and snowmelt are subject to interception. If that

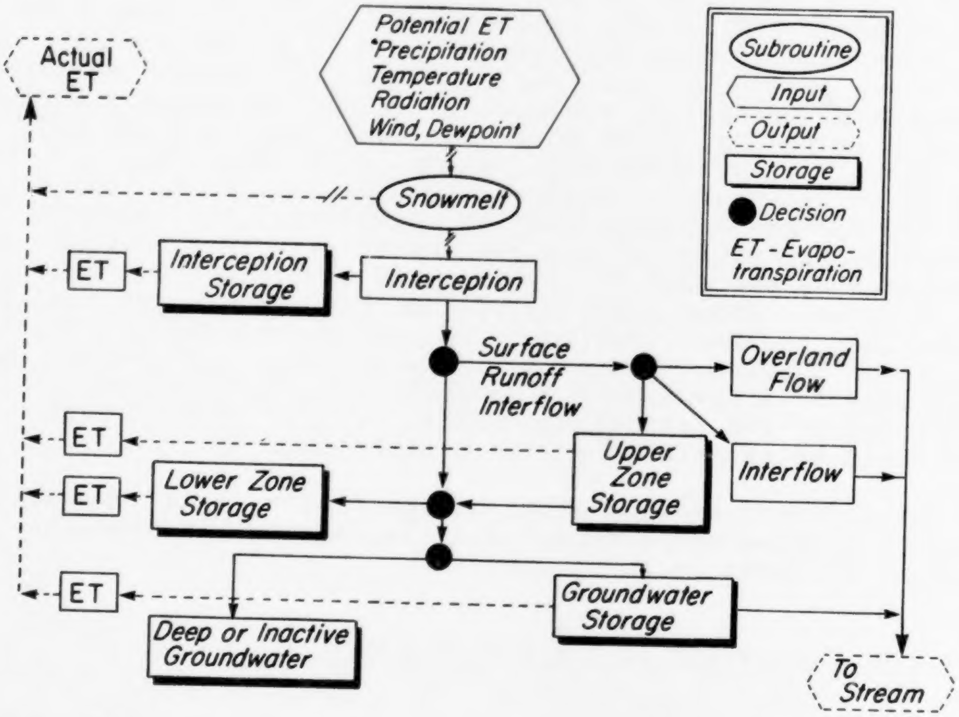

Actual ET
Potential ET
*Precipitation
Temperature
Radiation
Wind, Dewpoint
Subroutine
Input
Output
Storage
Decision
ET - Evapo-transpiration
Snowmelt
ET
Interception Storage
Interception
Surface Runoff Interflow
Overland Flow
ET
Upper Zone Storage
Interflow
ET
Lower Zone Storage
ET
Groundwater Storage
Deep or Inactive Groundwater
To Stream

Figure 8. Representation of the Hydrological Processes in a Pervious Land-segment (HSPF)

storage is full infiltration occurs. Infiltration capacity is a function of the storage in the lower zone and a parameter INFILT which reflects the permeability of the soil. Infiltrated moisture passes to the lower zone or to groundwater storage. Excess moisture either remains on the surface or enters flow paths leading to the upper zone or to interflow. Percolation from the upper zone to the lower zone and groundwater is modeled. The model regards overland flow as equivalent to that along a plane surface of length, slope and roughness specified by the user. It uses a kinematic method to calculate the overland flow rate. Other contributions to streamflow come from interflow and groundwater outflow.

Evapotranspiration (ET) can occur from any of the storages. The model algorithms compute the amount of ET from each storage, based on potential ET data supplied by the user.

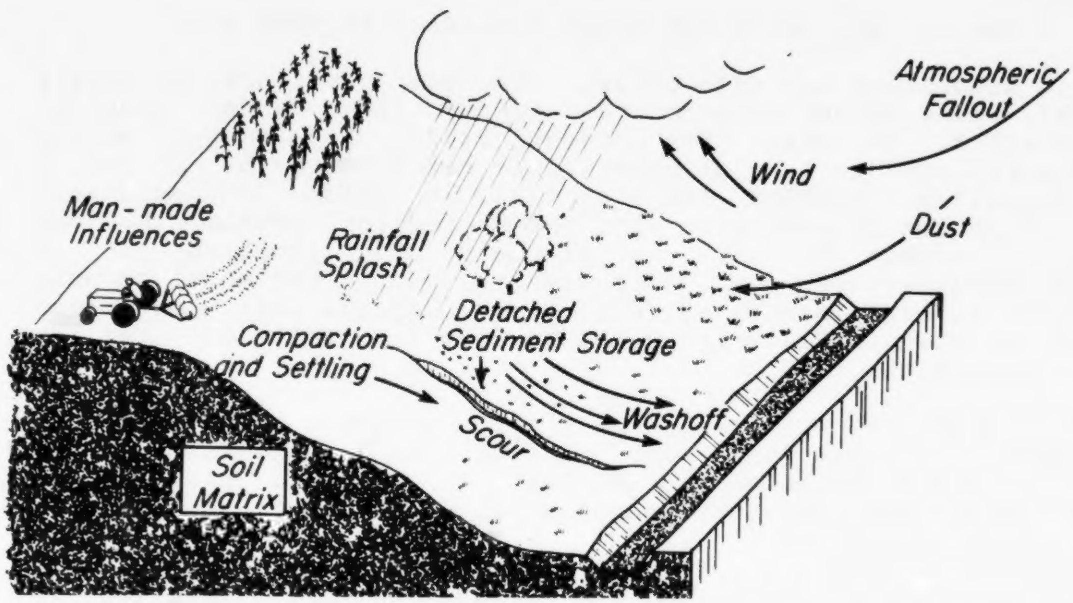
Sediment Simulation in the PERLND Module

The processes modeled in the SEDMNT section are shown in Figure 9. It also shows the simple equations used, which are based on one of the first continuous sediment simulation models (Negev 1967). The rate of detachment by rainfall is a power function of rainfall intensity, modified to account for protective cover (C) and any special management practices (SMPF) (e.g. terracing, contouring). SMPF corresponds to the factor P in the Universal Soil Loss Equation. Washoff (WS) is the removal, by overland flow, of detached material. It is modeled as a power function of overland flow, which is computed by the hydrology section (PWATER), but washoff is limited by the supply of detached material. This supply can be altered by the user at any time, to simulate the effect of soil tillage. Scour (SCR) is also modeled as a power function of overland (surface) outflow. This simulates direct erosion by surface outflow, such as gully formation. For scour, the model considers the supply of parent material unlimited. The coefficients and exponents (KRER, JRER, etc) must be determined by experience and/or calibration.

The sediment section also accounts for soil compaction (using a first-order process) and deposition or removal of detached sediment (e.g. by wind).

Pesticide Simulation in the PERLND Module

The procedures used to simulate pesticides were first developed for the Pesticide Transport and Runoff (PTR) Model


Atmospheric Fallout
Wind
Man-made Influences
Dust
Rainfall Splash
Detached Sediment Storage
Compaction and Settling
Washoff
Scour
Soil Matrix

Detachment: $DET = (1-C) * SMPF * KRER * RAIN^{JRER}$

Washoff: $WS = KSER * SURO^{JSER}$

Scour: $SCR = KGER * SURO^{JGER}$

Figure 9. Sediment-related Processes in a Pervious Land-segment, as Modeled in HSPF

(Crawford and Donigian 1973). Testing and refinement led to the Agricultural Runoff Management (ARM) Model (Donigian and Crawford 1976, and Donigian et al 1977). After further modifications these algorithms were included in the PERLND module of HSPF.

In this model, the soil is viewed as having four layers (Figure 10), corresponding to the surface, upper, lower and groundwater storages used in the hydrology section (Figure 8). The transport and reactions of pesticides are treated separately.

Transport rates for dissolved material are based on the internal and external fluxes (flows) computed in the hydrology section of the module. Soluble chemicals are transported down through the soil profile and are washed out into steams with surface runoff, interflow and groundwater flow. Sediment-associated pesticides (and nutrients) are removed from the surface layer whenever sediment washoff occurs.

The two pesticide reactions simulated by HSPF are:

1. Adsorption and desorption. The user can choose to handle this using either temperature-corrected first order reaction kinetics, in which the concentrations are always moving towards equilibrium but never quite reach it, or he can use a Freundlich isotherm (Figure 11), in which instantaneous equilibrium is assumed. With the Freundlich method, he can elect either to use a single-valued isotherm or a non-single-valued one. This was included in the model because there is experimental evidence which suggests that pesticides do not always follow the same curve on desorption as they do on adsorption.

2. Degradation. Although the actual mechanisms of degradation are many and complex, HSPF uses a simple first-order relationship to approximate this process. A different rate constant can be supplied for each soil layer.

Adsorption, desorption and degradation are simulated in each of the four soil layers (Figure 10). Different parameters can be used in each layer.

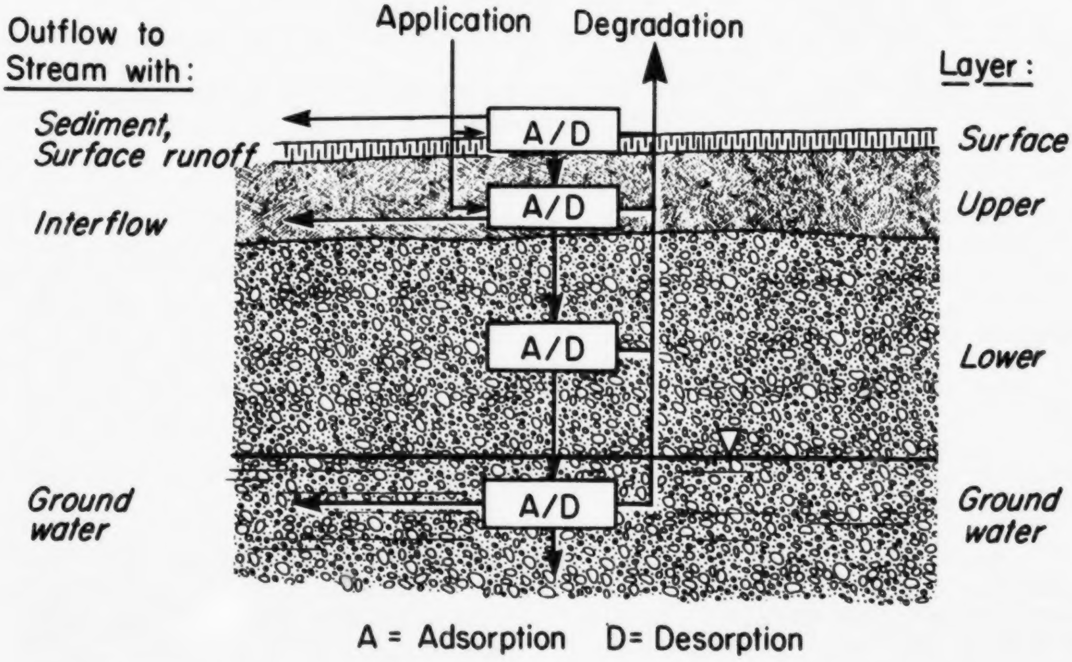

Outflow to
Stream with:
Application
Degradation
Layer:
Sediment,
Surface runoff
A/D
Surface
A/D
Upper
Interflow
A/D
Lower
Ground
water
A/D
Ground
water
A = Adsorption D= Desorption

Figure 10. Pesticide-related Processes in a Pervious Land-segment, as Modeled in HSPF

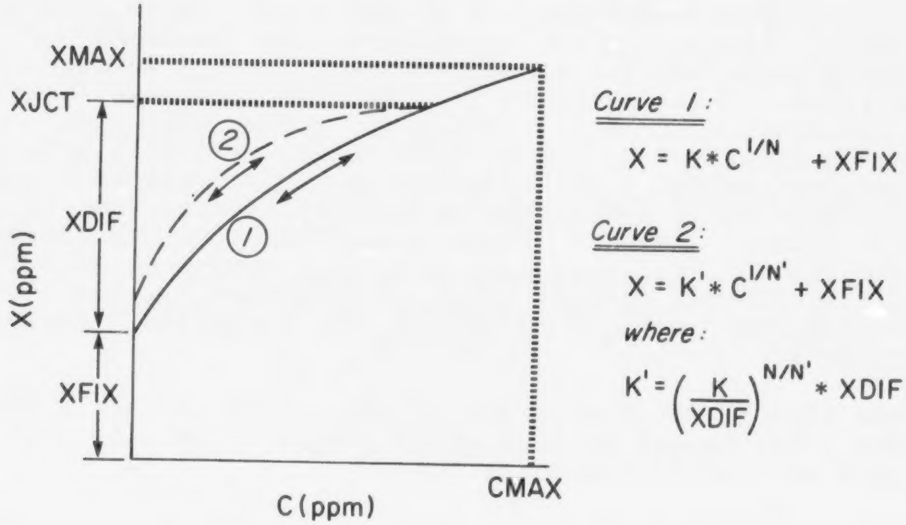


Figure 11. Single-valued and Non-single-valued Freundlich Isotherms, for Modeling Adsorption/Desorption

THE HSPF IMPERVIOUS LAND-SEGMENT (IMPLND) MODULE

This module is designed to simulate processes in areas where the ground is totally impervious; usually it is used on parts of urban areas. The computer code has a similar structure to that of the PERLND module (Figure 7), but has no agri-chemical sections and the other sections have been suitably modified. It is not designed to handle pesticides but one could simulate them as "general quality constituents" using module section 7, if required.

THE HSPF REACH/RESERVOIR (RCHRES) MODULE

General Comments

As the structure chart for this module shows (Figure 12), it is designed to simulate the transport and reactions of a wide variety of constituents in streams and lakes. Like the PERLND module, each section of the RCHRES module simulates a different set of processes, and the user can switch on that combination of sections which is best suited to simulate the constituents which he is studying. Most of the the other general comments made regarding the PERLND module are also applicable to the RCHRES module.

Section HYDR simulates the movement of water (hydraulic routing). Section HTRCH evaluates the exchange of heat between a reach and the atmosphere and, thus, simulates water temperature. These sections are important because transport and temperature greatly influence almost all the other processes simulated by the module. Sections SEDTRN and GQUAL simulate the movement of sediment and "generalized" quality constituents (e.g. pesticides). We will discuss them in more detail later. Section RQUAL simulates the "traditional" biochemical constituents, such as oxygen, biochemical oxygen demand, nutrients, phytoplankton, zooplankton, carbon dioxide and refractory organic products of biological death and respiration.

One significant limitation of the RCHRES module is that it assumes total mixing in the water body; thus it does not simulate stratified impoundments.

Hydraulic Routing in the RCHRES Module

HSPF uses a simple technique for flow routing. The catchment stream network is subdivided into "reaches" (Figure 4) and calculations start with the upstream ones. Each reach may have several outflows and each outflow rate may be a function of storage in the reach (storage routing) or a

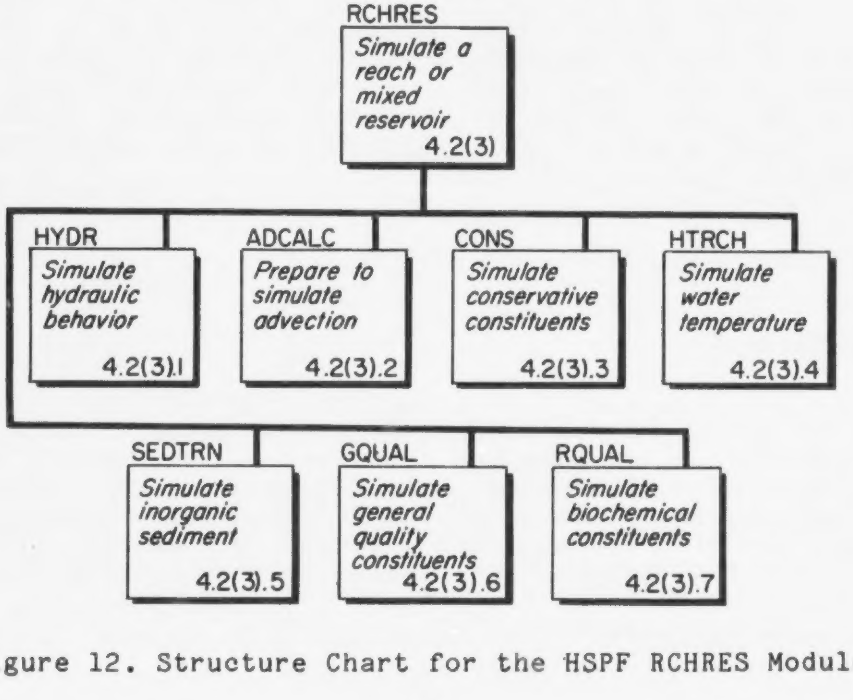

RCHRES
Simulate a reach or mixed reservoir
4.2(3)
HYDR
Simulate hydraulic behavior
4.2(3).1
ADCALC
Prepare to simulate advection
4.2(3).2
CONS
Simulate conservative constituents
4.2(3).3
HTRCH
Simulate water temperature
4.2(3).4
SEDTRN
Simulate inorganic sediment
4.2(3).5
GQUAL
Simulate general quality constituents
4.2(3).6
RQUAL
Simulate biochemical constituents
4.2(3).7

Figure 12. Structure Chart for the HSPF RCHRES Module

function of time (e.g. to supply demands of irrigators), or a combination of both.

HSPF can handle a reach network of any complexity; it can even handle situations where flows are split (diverted) and later recombined further downstream (e.g. through hydro-power diversion tunnels). Also, it can handle water bodies of any shape; for example, streams do not have to be represented with trapezoidal cross sections.

Sediment Routing in the RCHRES Module

The sediment routing method has been adapted from that used in the SERATRA model (Onishi and Wise 1979). Each reach is viewed as containing one "layer" of suspended, or entrained, sediment and one layer of bed sediment (Figure 13). Three classes of sediment are handled - sand, silt and clay. Each is separately routed through the reach and its deposition or erosion rate is calculated.

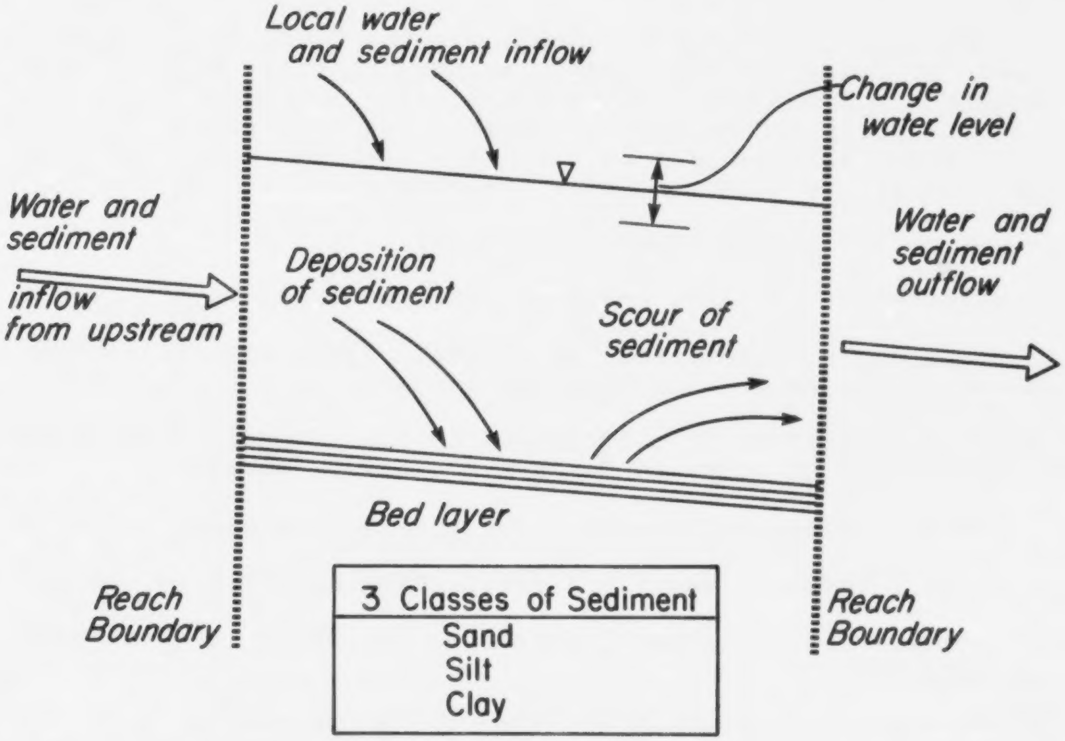

Local water
and sediment inflow
Change in
water level
Water and
sediment
inflow
from upstream
Deposition
of sediment
Scour of
sediment
Water and
sediment
outflow
Bed layer
Reach
Boundary
3 Classes of Sediment
Sand
Silt
Clay
Reach
Boundary

Figure 13. Sediment Processes Considered in the RCHRES Module of HSPF

For sand, the transport capacity is first calculated using either the Colby (1964 a and b), or Toffaleti (1968 and 1969) method, or a user supplied power function of velocity. If the calculated transport capacity exceeds the load present scour is simulated and if the opposite is true deposition is simulated.

For silt and clay, the critical shear stress concept is used. If the critical shear stress for scour is exceeded, scour takes place. On the other hand, if the actual shear stress is less than the critical value for deposition, deposition occurs. For intermediate values of shear stress, the bed is stable.

Pesticide and Toxic Substance Simulation in the RCHRES Module

Pesticides and many other toxic substances are subject to a variety of processes in the aquatic environment (Figure 14). In the RCHRES module, such compounds are called "generalized quality constituents" and they are simulated using module section GQUAL (Figure 12).

The algorithms used by module section GQUAL are, again, based on those incorporated in the SERATRA model. The processes included are shown schematically in Figure 15. The model assumes that the chemical must exist in solution and is, thus, potentially subject to all the processes shown on the left side of the figure. These include:

1. movement with the water (advection).

2. hydrolysis. A first order pH-dependent equation is used.

3. oxidation by agents such as singlet oxygen and alkylperoxy radicals. A second order equation is used.

4. volatilization. This is linked to the oxygen reaeration rate which can be computed using a variety of equations.

5. biodegradation. A second order equation is used.

6. other methods of decay. A first order equation is used.

7. formation of "daughter" products by decay of "parent" compounds.

The user decides which of the above processes will be simulated (active); he need only supply input for those that are active. In this connection, note that:

1. all of the above decay rates can be adjusted for temperature.

2. much of the supplementary input required for these processes (e.g. biomass concentrations, free radical concentration) can be supplied either as time series, or as monthly cyclic data, or single fixed values.

If the user specifies that the chemical is sediment-associated, then all the processes shown on the right of Figure 15 also become active:

1. Adsorption and desorption between the solution phase and sand, silt and clay in suspension and on the bed. First-order rection kinetics are used.

2. Transport of adsorbed material with the sediment. This includes advection, scour and deposition.

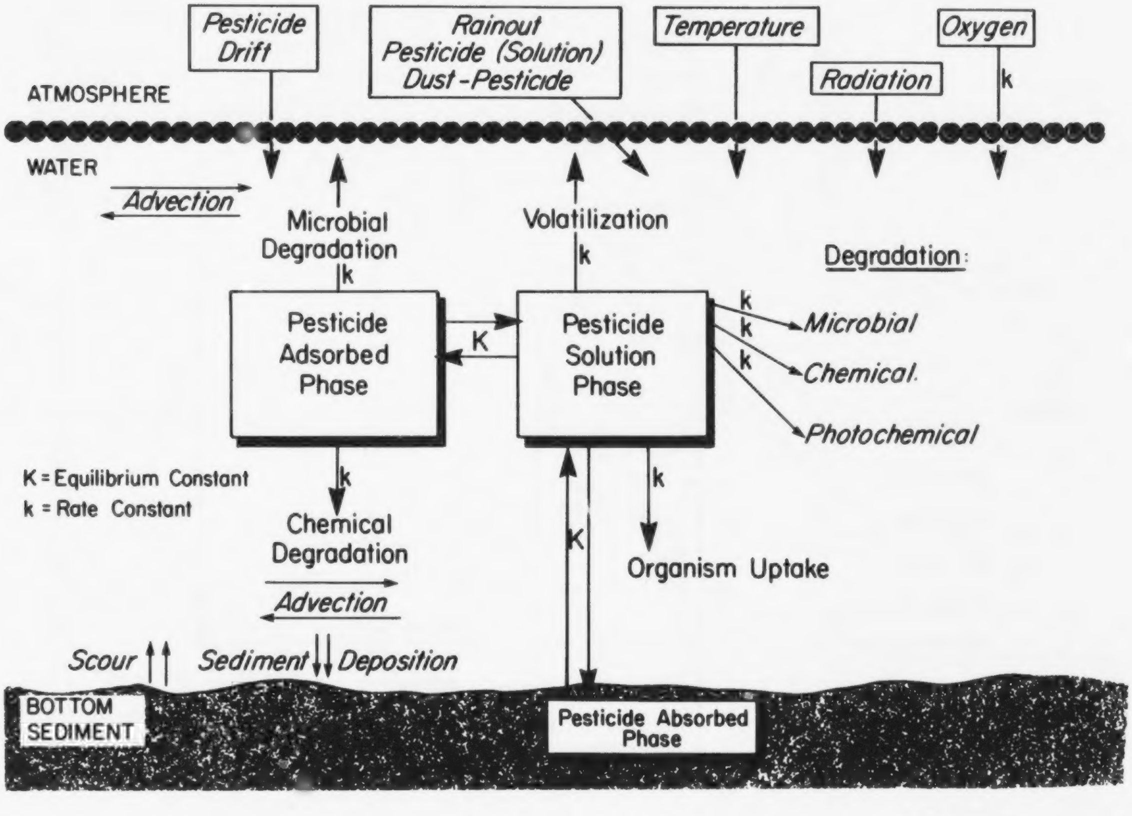

Pesticide Drift
Rainout Pesticide (Solution) Dust-Pesticide
Temperature
Oxygen
Radiation
k
ATMOSPHERE
WATER
Advection
Microbial Degradation
k
Volatilization
k
Degradation:
Pesticide Adsorbed Phase
K
Pesticide Solution Phase
k
k
k
Microbial
Chemical
Photochemical
K = Equilibrium Constant
k = Rate Constant
k
Chemical Degradation
Advection
K
k
Organism Uptake
Scour
Sediment
Deposition
BOTTOM SEDIMENT
Pesticide Absorbed Phase

Figure 14. Pesticide Transport and Transformation Processes in Flowing Streams

3. Decay of adsorbed chemical, modeled as a first-order process.

THE CREAMS MODEL

General Comments

This model, developed by scientists in the U.S. Department of Agriculture (USDA) is documented fully in "CREAMS: A Field Scale Model for Chemicals, Runoff and Erosion from Agricultural Management Systems" (Knisel 1980). For the sake of brevity, we will refer to that publication from now on as the "CREAMS Report."

The goal of the developers of this model was to assemble, in one year, a program that:

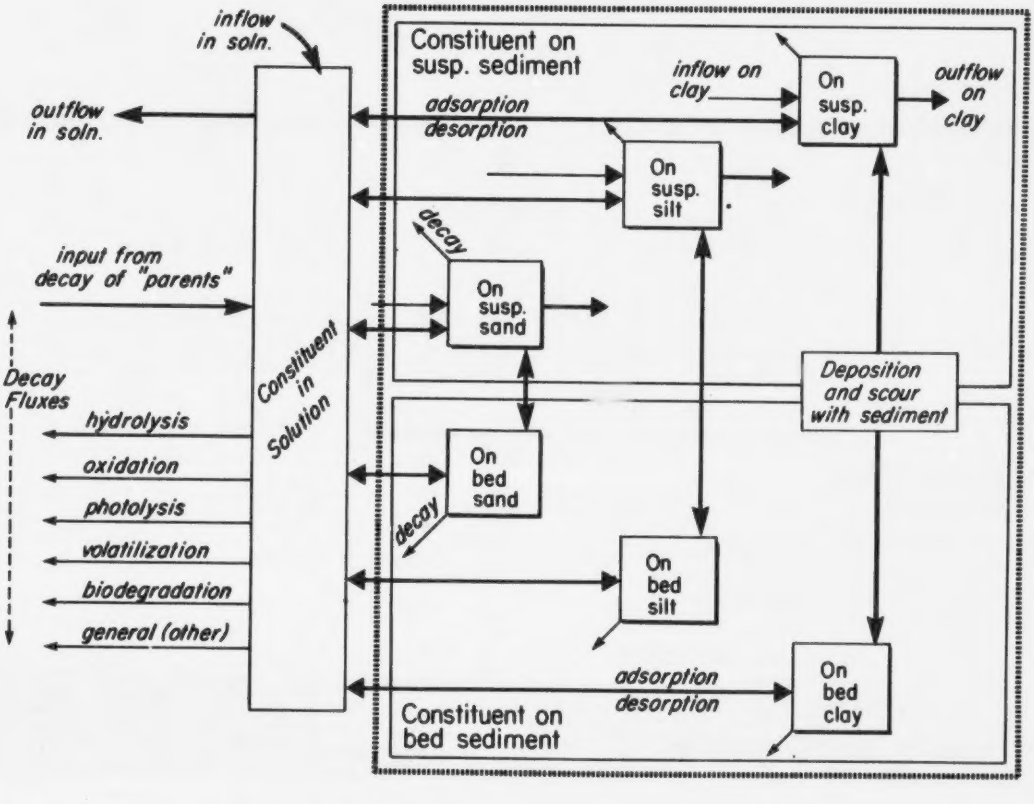

inflow in soln.
outflow in soln.
input from decay of "parents"
Decay Fluxes
hydrolysis
oxidation
photolysis
volatilization
biodegradation
general (other)
Constituent in Solution
Constituent on susp. sediment
adsorption desorption
inflow on clay
On susp. clay
outflow on clay
On susp. silt
decay
On susp. sand
Deposition and scour with sediment
On bed sand
decay
On bed silt
adsorption desorption
On bed clay
Constituent on bed sediment

Figure 15. Simulation of a "Generalized Quality Constituent" in HSPF

1. would simulate field-size areas. The development of a model that could handle the groundwater and stream components of the hydrological cycle and thus, would simulate an entire catchment, was deferred to a later time.

2. was physically based and reasonably accurate, yet simple enough to be easily understood

3. had as few parameters as possible and required a minimum of calibration.

4. included runoff, percolation, erosion and dissolved and adsorbed plant nutrients and pesticides.

5. was directly applicable to the study of alternative agricultural management practices (e.g. terracing, contouring, minimum tillage).

To meet their very short time-table the USDA scientists did not attempt to develop an entirely new system; they merged and improved models that they already had. The result (CREAMS) is a model with three components, for hydrology, sediment yield and chemicals (Figure 16). Like the modules in HSPF, these components can be run independently. For example, a user may simulate the hydrological behavior of a field and store the results. In a subsequent run he might simulate sediment and/or chemicals using for input either the simulated runoff data or observed data, if it is available.

Hydrological Simulation in the CREAMS Model

Like most modern deterministic hydrological models, CREAMS uses a moisture accounting procedure. It has a simple snow simulation algrorithm. It offers two options for surface runoff. The SSC Curve number model is used if only daily rainfall data are available; if hourly data are available, an infiltration-based model is used. Infiltration of snowmelt and rainfall into the soil is estimated using a development of the Green and Ampt model. Soil moisture is accounted for using two storages (Figure 17):

1. A shallow zone which, through its degree of saturation, controls infiltration.

2. A root zone, which extends down to the maximum rooting depth of the crop. Moisture that percolates below this zone is called seepage and is one of the outputs of the model.

Despite the fact that it has only two soil moisture storages this is indeed a physically based model. The algorithms used to simulate infiltration, plant growth, evapotranspiration and overland flow are sophisticated and are based on extensive prior research, and have been tested using much data from watersheds operated by the USDA.

The methods used in CREAMS differ from HSPF in many respects. One very significant example is that, whereas HSPF uses a constant time step (e.g. 15 minutes), CREAMS uses the storm as the basic time unit. It estimates the total runoff

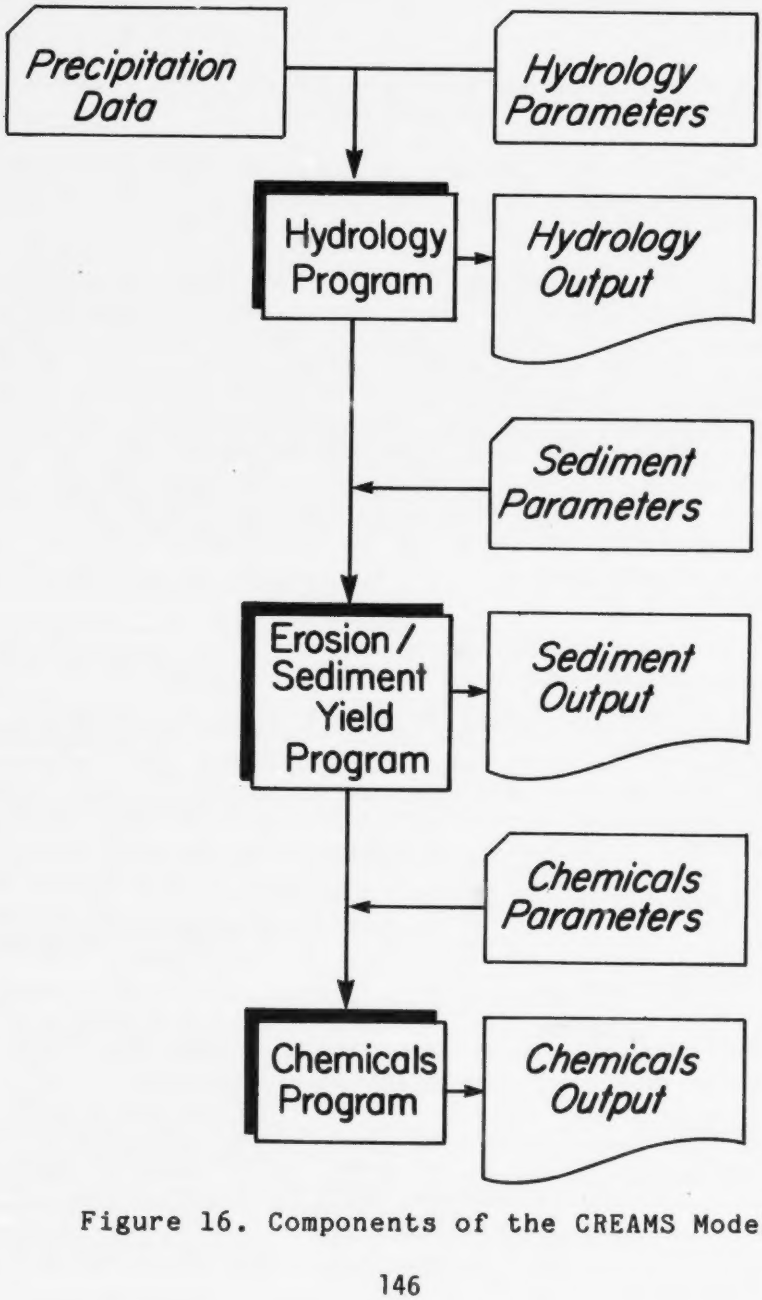

Precipitation Data
Hydrology Parameters
Hydrology Program
Hydrology Output
Sediment Parameters
Erosion / Sediment Yield Program
Sediment Output
Chemicals Parameters
Chemicals Program
Chemicals Output

Figure 16. Components of the CREAMS Model

and the peak rate of runoff for the entire storm event, and does not attempt to simulate the runoff for a series of constant time intervals during the storm.

Simulation of Erosion and Sediment Yield in the CREAMS Model

Sediment simulation is a very important component of any model designed to simulate agricultural lands. It is especially important if the model is to be directly applicable to the study of alternative management practices, such as contouring, terracing and ponding. Therefore, the developers of CREAMS went into great detail to represent the erosion, transport and deposition processes that take place on farmed areas. For sediment simulation, they regarded a field as a combination of three basic element types (Figure 18):

1. Overland flow. This includes both rill, and inter-rill areas. Erosion is simulated using equations developed from the Universal Soil Loss Equation (Wischmeier and Smith 1978) and the modeling of transport is based on the work of Yalin (1963). The user can specify whether the slope is uniform, concave, convex, or some combination, and the model routes sediment through the various sub-elements, computing erosion, transport and deposition in all of them.

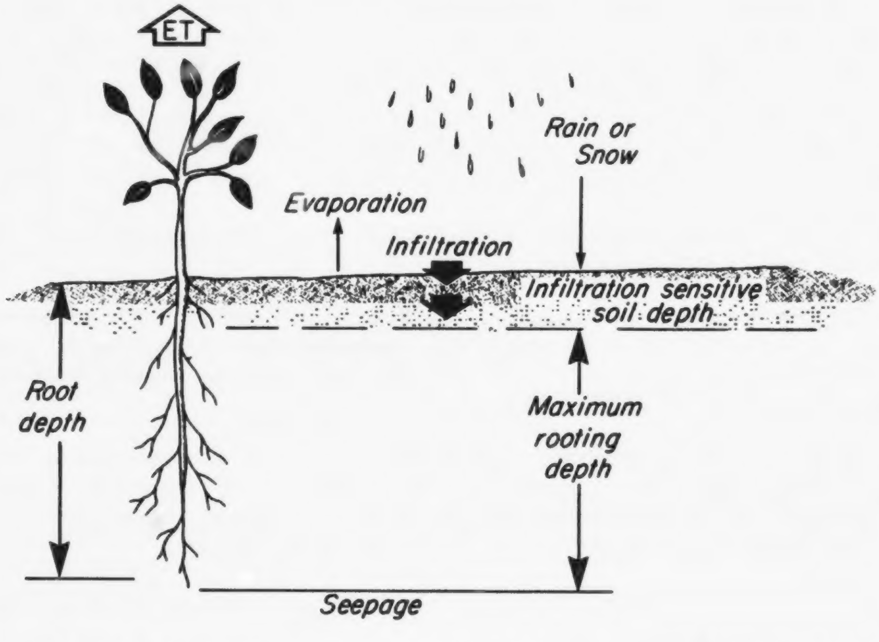


Figure 17. Soil Moisture Zones Used in the CREAMS Hydrology Program

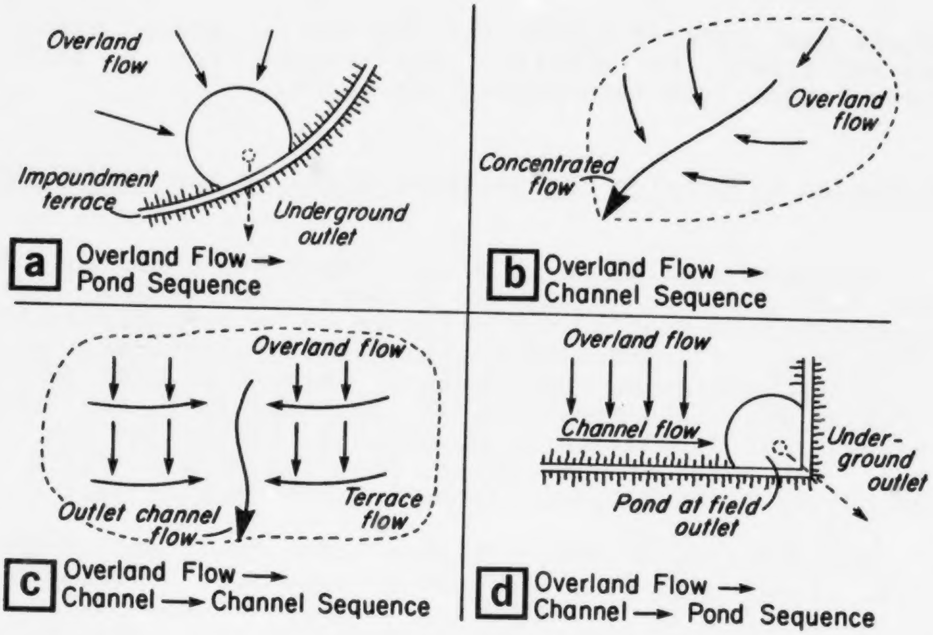

Overland flow
Impoundment terrace
Underground outlet
a
Overland Flow →
Pond Sequence
Concentrated flow
Overland flow
b
Overland Flow →
Channel Sequence
Overland flow
Outlet channel flow
Terrace flow
c
Overland Flow →
Channel → Channel Sequence
Overland flow
Channel flow
Underground outlet
Pond at field outlet
d
Overland Flow →
Channel → Pond Sequence

Figure 18. Representation of Typical Field Systems in the Sediment Component of CREAMS

2. Channel. This represents flow in areas with very concentrated flow such as terrace channels, but not gullies. The model simulates spatially varying flow, to account for backwater effects due to restricted outlets. It breaks the element into several computational segments and simulates detachment, transport and deposition of sediment along each one.

3. Pond. This element simulates the trapping of sediment behind small impoundments.

To represent a field, the user "chains" several of the above elements in a specified sequence. In this way, the commonly used agricultural practices can be represented quite realistically (Figure 18).

The CREAMS sediment simulation is very much more detailed than that in HSPF. Besides the detail discussed above, it considers five distinct classes of sediment (Figure 19) and routes them all separately through the field.

Pesticide Simulation in the CREAMS Model

Pesticide behavior is modeled by CREAMS as follows (Figure 20):

1. It simulates the interception of pesticides by vegetation and the subsequent degradation on the foliage before the chemical is washed off (to the land surface) by rainfall. HSPF does not include these processes.

2. It assumes that a layer of soil only 1 cm thick is active when pesticide is leached from the soil by surface runoff. Processes further underground are not considered. HSPF uses four layers, extending all the way to the groundwater.

The following processes, in the surface soil layer, are considered:

1. Leaching of dissolved pesticide by surface runoff.

2. Vertical movement of dissolved pesticide from the surface layer, with percolating soil moisture.

3. Adsorption and desorption, using a linear isotherm with constant partition coefficient (Kd). HSPF has three options for simulating adsorption/desorption.

CREAMS MODEL

SEDIMENT CHARACTERISTICS ASSUMED FOR DETACHED SEDIMENT BEFORE DEPOSITION

PARTICLE TYPE	DIAMETER	SPECIFIC GRAVITY	FRACTION OF TOTAL AMOUNT (MASS BASIS)
	(MM)	(G/CM^3)	
PRIMARY CLAY	.002	2.60	.05
PRIMARY SILT	.010	2.65	.08
SMALL AGGREGATE	.030	1.80	.50
LARGE AGGREGATE	.500	1.60	.31
PRIMARY SAND	.200	2.65	.06

Figure 19. Classes of Sediment Represented in the CREAMS Model

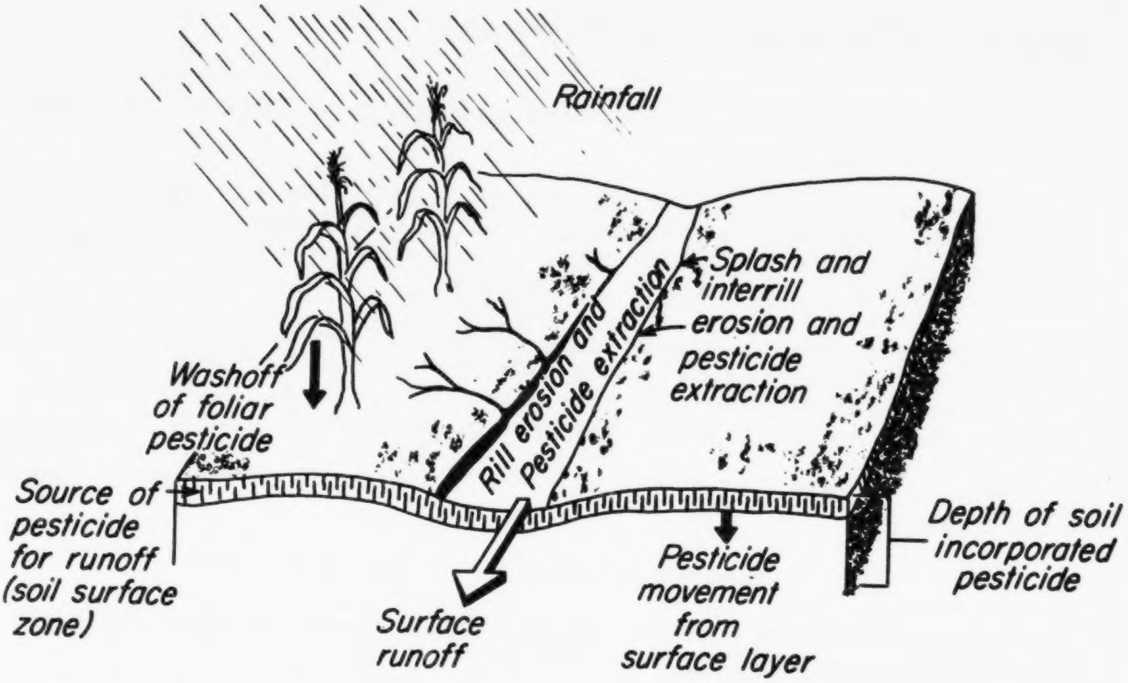

Rainfall
Splash and interrill erosion and pesticide extraction
Rill erosion and Pesticide extraction
Washoff of foliar pesticide
Source of pesticide for runoff (soil surface zone)
Depth of soil incorporated pesticide
Pesticide movement from surface layer
Surface runoff

Figure 20. Pesticide Transport Processes Modeled in CREAMS

4. Washoff of pesticide adsorbed on sediment. This component of the model uses an "enrichment factor," to account for the fact that sediment leaving the field is usually of finer composition than the parent material and, therefore, will contain a higher concentration of adsorbed pesticide. HSPF does not use an enrichment factor.

The CREAMS report has a good discussion of the performance of its pesticide component. The test results were, apparently, quite good but the following observations were also made:

1. Because the model only updates the concentration of runoff-available pesticide once per storm (at the end), it tends to over-predict pesticide yield for severe storm events. To us, it seems that this is one disadvantage of simulating the entire storm in one time step, rather than using a constant time step.

2. It has been observed that pesticide desorption from soil is non-linear and becomes more difficult with time. However, the CREAMS model developers do not believe that sufficient experimental data have been acquired to warrant changing their simple adsorption/desorption method.

Some Further Comparisons Between CREAMS and HSPF

The documentation of the two models is very different:

1. The CREAMS report is very comprehensive. In the introduction there is a good review of many different agricultural chemical models. The report also discusses thoroughly:

a. the physical processes which the model was designed to simulate

b. the equations used in the code.

c. results of testing work and sensitivity analysis for the parameters

In addition, the report contains a user's manual, which describes the input required to run the model, and methods for estimating parameter values. It also includes much supplementary documentation -- papers written on specific aspects of the model.

2. The HSPF report is also a lengthy document, but is very different. It systematically describes the computer code, explaining the algorithms used. It also documents very logically the input required to run the model. However, it does not give a great deal of background material in the algorithm descriptions, nor does it suggest methods for evaluating parameters. Readers are referred to other sources, such as the ARM Model Users Manual (Donigian and Davis 1978) for such information.

In summary, the HSPF code and documentation are extremely systematic, while the CREAMS documentation is very detailed.

A key difference between HSPF and CREAMS is that the former model is based on continuous simulation using a constant time step, whereas the latter model is "event based." CREAMS calculates values such as runoff volume and peak runoff rate for each storm and uses a coarse time step between storms to account for factors such as the gradual drying of the soil and pesticide degradation.

THE EXAMS MODEL

General Comments

The Exposure Analysis Modeling System (EXAMS) was recently developed at the Environmental Research Laboratory in Athens, Georgia and is documented in a very comprehensive report (Burns, Cline and Lassiter 1981). Our discussion of this model is brief because it will be discussed in other papers at this conference.

Basically, EXAMS is a hazard evaluation system. Its purpose is to permit a scientist to make a rapid assessment of the likely long-term behavior of a chemical in a waterway system, assuming it enters the system at an approximately constant rate. It is intended for use as a "screening tool." A company wishing to market a new chemical must supply the U.S. government with data on the properties of the compound. EXAMS can make use of these data to estimate the likely long-term effects of the chemical and can, thus, assist in the licensing process.

EXAMS is limited to the stream and lake phases of the hydrological cycle. As in HSPF, the stream system is broken down into a series of elements, called "compartments." EXAMS includes four "compartment types."

1. Epilimnion. This represents well-mixed water bodies such as streams and the upper layer of lakes.

2. Hypolimnion. This represents the lower levels of lakes.

3. Benthic. Bottom sediments

4. Littoral. This represents the shallow borders of a water body, where there is very little transport.

As with HSPF, the user models his stream/lake system by chaining together a set of compartments. Note that a single water body, such as a lake, may be represented by several compartments, usually of different types.

The EXAMS model focusses on the chemical itself; other aspects of the water system are not modeled in detail. For example, the model assumes that the flow rates are steady and, similarly, that environmental factors such as temperature and pH are constant. With these factors and the chemical loading rate specified by the user, EXAMS simulates the behavior of the chemical under investigation. The results of this work are estimates of:

1. exposure. The model determines the long-term "expected environmental concentrations" (EECs) in each compartment.

2. fate. The model shows how much of the chemical has been lost from a compartment by the various processes of transport and reaction.

3. persistence. The model indicates how rapidly the concentrations in each compartment would decrease if loading suddenly stopped.

EXAMS is an interactive computer program. The user keeps data concerning various typical aquatic environments on computer files. To run the program, he need only specify the "environment" file and then answer a set of questions concerning the chemical properties of the compound. The procedure can be repeated very rapidly for a set of different environments, thus enabling him to assess the effects that the proposed chemical would have in various different climatic regimes.

Simulation of Transport Processes in EXAMS

This is very simple. The model assumes that the volumes of all the compartments remain constant. Then, based on data concerning the (steady) hydrologic, sediment and chemical loadings into each compartment, it computes the movement of water and sediment through the system. The chemical under study travels with the water, sediment and phytoplankton.

EXAMS also models the processes of diffusion between compartments and the loss of chemical through valatilization and seepage through the bed.

Simulation of Chemical Reactions in EXAMS

Because the purpose of EXAMS is to predict the fate of complex chemicals using basic (laboratory) data concerning their properties, the typical reactions of organic compounds are represented in great detail; much more than in the HSPF model.

Ionization and sorption constrain the other (transformation) processes in the EXAMS model. Up to 15 different products of ionization (species) of a single compound can be handled. This permits the very different reactive properties of each species to be represented.

Sorption on sediment and two classes of biomass (resident and transported), is modeled, using instantaneous equilibrium with a linear isotherm.

The transformation processes modeled by EXAMS include photolysis, hydrolysis, biolysis, and oxidation. The methods used are similar to those in HSPF, but more detailed. Most reactions are represented by second-order equations, in which the reaction rate depends on both the concentration of the chemical and the value of some environmental variable, such as the concentration of biomass responsible for biolysis. Temperature effects are simulated using Arrhenius relationships.

CONCLUDING REMARKS

We have described and, to some extent, compared three models, recently developed in the U.S.A., for simulating the behavior of pesticides in the soil and stream environments. Our goal was to provide a concise summary of the capabilities of each model; not to try to judge their relative merits. Indeed, it is impossible to say that one model is "better" than the others; each one is best suited to its own type of application. In this connection, it should be remembered that the models are constantly being improved and extended. Thus, any remark concerning an alleged shortcoming in a model could quite soon be out of date.

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This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

MODELING THE BEHAVIOR OF PESTICIDES USING THE ARM MODEL

by

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INTRODUCTION

Under the US-USSR joint project "Forms and Mechanisms by Which Pesticides and Chemicals Are Transported", it has been recognized as advisable to develop and introduce simulation models of dynamic type which describe the behavior of pesticides in soil(I,2,4,II-I3) . It is known that these models are based on a description of hydrology of an agricultural watershed.

In calculations of the total water balance,one uses time series of hydrometeorological data,such as rainfall,evaporation, wind velocity, dew point, net radiation, maximum and minimum air temperature(daily values), as well as watershed topography, initial moisture storages,the extent of plant coverage and condition of the soil surface.

A hydrologic model has submodels which describe "solid" runoff formation and the processes of sorption and degradation, and permit the mass balance of a pesticide in the watershed to be calculated. After calibration with respect to a number of hydrometeorological observations and determination of the parameters of sorption and degradation, the ARM model can be used as a predictive one.

The purpose of this study was to test the ARM model in various soil-climatic zones of the Europian part of the Soviet Union.

The study involved the following stages:

- realization of the model on the Soviet computer system EC;
- selection of experimental watersheds;

- design and instrumentation of small experimental plots to study pesticide degradation kinetics using the method of isotope indicators;
- acquisition of characteristic parameters,for example, sorption isotherms for various pesticides and soil conditions;
- accumulation in a data base of the data on a continuous monitoring of hydrometeorological parameters;
- verification of the ARM model for areas of various scales, sensitivity analysis of the selected parameters of the model and determination of errors.

REALIZATION OF THE MODEL ON THE COMPUTER SYSTEM EC

While introducing the ARM model,we consulted with the leading scientists of the U.S. EPA Environmental Research Laboratory (Athens,Georgia), and received the technical documentation and model texts on magnetic tapes. Nevertheless,introducing even the completely developed model is a very serious scientific problem that involves primarily its realization on the Soviet computer system, testing under field conditions and elaboration of recommendations on its use in specific soil-climatic zones.

The model is a large, relatively complex computer program comprised of I5 major subroutines and more than 5700 executable source statements written in the FORTRAN IV language. Much of the model testing has been performed on an IBM 370/I68 at Stanford University(I3) . On the IBM 370/I68 using the FORTRAN H compiler, the program requires approximately 360K bytes of storage. Program execution after its compilation in a simple structure requires up to 230K bytes of storage depending on the model options selected. Thus, a computer with a large storage capability is needed for using the ARM model. Realization of the model on EC-I050 required certain changes associated with the specific features of this computer. To reduce the required storage capacity we organized an overlay structure of the program by its dividing into segments according to functional relations between the program sections. Fifteen modules were grouped into four segments.

The overlay program is not loaded to the main storage in whole. Only one program section, or root segment,remains invariably in the storage,while the rest segments change each other as the program is executed. In the overlay structure, the program execution on EC-I050 requires up to I50K bytes of storage. The program can be used on other computers of the EC type. Incoming texts of the ARM model are stored in consequtive magnetic tape files at various levels. In addition, there are operating files on magnetic disks that are used for modification of individual submodels in the dialog mode of operation.

EVALUATION OF CHARACTERISTIC PARAMETERS OF THE MODEL

Regarding the way of its realization, the ARM model is a simulation one. It uses a set of empirical relations and rather artificially takes into account a spatial inhomogeneity of a watershed that is given by an integral function of infiltration. Therefore, prior to the evaluation of the characteristic parameters of the model, its hydrological part is calibrated according to the technique described in (II-I3) . Following the hydrological calibration to obtain water balance, we calibrate "solid" runoff and evaluate the characteristic parameters of the model.

Accuracy of pesticide mass balance calculations depends mainly on an accurate evaluation of coefficients entering into the equations. Because of a very important role of sorption in pesticide transport, it is necessary first of all to determine coefficients of the sorption isotherms. To obtain the sorption isotherms for the watersheds studied, samples were collected from the wells in the upper, middle and low parts of the slopes. Then a set of experiments on ^{14}C-labelled BHC was carried out to measure the sorption isotherm parameters in various layers. Activity of an equilibrium solution separated from the soil by centrifugation was determined radiometrically five days later, using "MARK-II" scintillation radiometer with a dioxan scintillator. The technique developed specially for these purposes was described in(9) . Results of the sorption study are given in Table I. Not only the parameters of the sorption submodel were obtained from the above results but also the relation between the isotherm parameters and physical-chemical properties of the sandy soddy podzolic soil. Processing the results presented gave the following relationship between the degree of sorption and the content of organic matter C_{total}:

$$K_F = 7.5 \cdot C_{total}^{I.I25}$$

Here K_F is the parameter of Freundlich isotherm

$$[P]_S = K_F \, [P]_W^{I/N} \quad ,$$

where $[P]_S$ and $[P]_W$ are the pesticide concentrations in soil and water, respectively.

Differences in the degree of pesticide sorption correlated with a layer-by-layer distribution of organic matter. Percentage of labelled BHC desorption was insignificant and ranged from 5 to I2% for the samples collected, thus indicating that the sorption was almost irreversible.

A major part of sorbed BHC (about 80%) was found in particles less than 0.00I mm in size.

Table I. Average physical-chemical properties of soils studied and average parameters of Freundlich isotherms for ^{14}C-labelled BHC

Layer properties	Sampling depth, cm				
U	0–20	20–30	20–40	20–50	67–75
I	2	3	4	5	6
Bulk weight, g/cm^3	I.3±0.I	I.3±0.I	I.4±0.I	I.4±0.I	I.5±0.02
Specific weight, g/cm^3	2.5±0.07	2,5±0.06	2.6±0.04	2.7±0.04	2.7±0.06
Total porosity in percent of the soil volume	49.8	47.6	46.8	46.8	42.6
Mechanical analysis of fine earth in percent of the weight					
Sand I - 0.25 mm	64.8	56.6	56.2	62.8	I6.2
0.25- 0.05 mm	I8.I	28.I	33.5	20.I	22.8
< 0.05 mm	I4.5	I4.7	8.4	I4.0	59.0
0.05- 0.0I mm	5.6	5.6	3.2	6.7	34.4
Dust < 0.0I mm	8.9	9.I	5.2	7.3	24.6
0.0I- 0.005 mm	I.0	I.0	0.4	0.9	6.9
0.005-0.00I mm	0.6	I.7	0.4	0.5	8.0

Table I (continued)

I	2	3	4	5	6
Silt < 0.00I mm	7.3	6.4	4.4	5.9	9.7
Treatment loss in percent of the weight	2.6	0.6	I.9	3.I	2.0
Hygroscopic moisture,%	0.8	0.9	0.3	I.I	I.7
Humus content,according to Tyurin,%	2.I±0.2	I.9	0.5	0.5	0.6
Total exchange bases, according to Kappen-Gikovits, mg·equiv./I00g	8.3±2.7	4.3±I.4	I.8±I.3	2.28±I.2	5.4±2.7
Hydrolytic acidity, mg·equiv./I00 g	2.3±0.7	2.0±0.8	I.4±0.8	I.4±0.6	I.3±0.4
pH water	6.I±0.7	5.8±0.6	5.7±0.4	5.7±0.6	5.6±0.4
pH salt	5.4±0.9	5.I±0.2	4.9±0.6	5.I±0.5	4.7±0.4
Al^{3+} according to Sokolov, mg·equiv./I00 g	0.I±0.04	0.02±0.0I	0.08±0.05	0.47±0.2	0.I±0.02
H^{+}	0.04±0.0I	0.03±0.0I	0.04±0.0I	0.05±0.2	0.04±0.0I
Adsorption of C^{I4}-labelled BHC					
K_R	I8.5±2.5	I8±I.7	3.2±0.4	3.2±0.3	2.5±0.2
I/N	0.94±0.05	0.94±0.05	0.95±0.0	0.94±0.03	0.94±0.03
Desorption in percent of the initial mass of sorbed labelled BHC	5.2±0.7	6.6±I.4	5.I±0.6	7.2±I.0	I0.2±0.8

Distribution of BHC and humus in various granulometric fractions of the Valdai soils is presented in Table 2. A high degree of participation of fine soil fractions in BHC adsorption can be accounted for not by a high content of these fractions in the soil, but by a high concentration of sorbed BHC in them. The latter exceeds by an order of magnitude or more the concentration of sorbed BHC in the soil as a whole. In its turn, a high sorption capacity of the fine fractions with respect to BHC can be accounted for by their increased humusness (I4). The character of humus and BHC distribution in fractions is almost the same.

Table 2. Distribution of BHC and humus in various granulometric fractions of the Valdai soil

Particle size, mm	Distiribution in fractions, %	
	Humus	BHC
0.0I - 0.05	3,4	7,4
0.005 - 0.0I	5.7	9.2
0.00I - 0.005	2.6	I.3
≤0.00I	88.6	82,I

In October I979, we began to carry out experiments on ^{I4}C-labelled BHC at the Valdai station for water-balance investigation(9) to study the kinetics of BHC degradation. Table 3 shows contributions of evaporation and chemical and microbiological degradation to ^{14}C-labelled BHC degradation. The amount of ^{14}C-labelled BHC applied to the soil is taken as unity.

RESULTS OF MODEL DEVELOPMENT AND TESTING UNDER FIELD CONDITIONS

To test the ARM model in various soil-climatic zones we selected two types of water regime of soils - pervious and impervious(3), and four experimental plots where the water balance was observed for many years. The pervious water regime,i.e. when evaporation is less than water infiltration to the soil, and the soil depth undergoes annually a thorough wetting up to the ground waters for many years, was observed at the Valdai and Trans-Carpathian stations for water-balance investigation (5,6). Mean annual rainfall in the Trans-Carpathian region

Table 3. Contributions of evaporation and chemical and microbiological degradation to the degradation of ^{14}C-labelled BHC

Days	Evaporation and chemical degradation	Chemical degradation	Evaporation and chemical and microbiological degradation	Chemical and microbiological degradation
2	0.I7	0.I3	0.I8	0.04
3	0.28	-	0.22	-
I5	0.4I	0.I5	0.4I	0.22
45	0.7I	0.37	0.72	0.35
67	0.78	0.53	0.79	0.54
II0	0.77	0.50	0.84	0.60

(brown forest soils) is 800-I000 mm at an evaporating capacity 600 mm, and in the Valdai (sand podzolic soils) 600-800 mm at an evaporating capacity 300-400 mm. The impervious water regime,i.e. when almost the whole of moisture accumulated in the soil reenters the atmosphere through evapotranspiration has been observed at the Moldavian station for water-balance investigation since I954 (7). Mean annual rainfall in this area (calcareous clay loamy chernozems) is about 500 mm. Based on the data of continuous hydrometeorological monitoring carried out at these stations for many years we calibrated the hydrological part of the ARM model, using the calibration technique described in (II-I3). Following the general hydrological calibration of the model and calculation of the water balance we calibrated the submodels of "solid" runoff and pesticide behavior.

As an example, we shall consider the components of pesticide mass balance obtained at the Moldavian station for water-balance investigation in Baltsat. The intensity of the processes of slope erosion depends on three factors: rainfall intensity, soil erodibility, and protective action of plant cover. Various combinations of these three factors were studied at four runoff plots in Baltsat from June 6 to September I2,I980. Characteristics of the experimental plots are given in Table 4. Commercial BHC (2 kg per 0.8 hectare) was applied on June 6, I980. In the period under study, there occurred about 70% of

Table 4. Characteristics of the experimental plots

Runoff plot number	Location	Average slope,%	Exposure	Type of land	Prevalet type of soil*
I	Baltsata Brook Middle part of the left slope,I40 m from the meteorological station	202	SW	Fallow (plowed on June 5)	Calcareous medium-deep clay-loamy chernozem on loam
2	Same as above	202	SW	Kidney beans	Same as above
3	Stantsionnyi Ravine Middle part of the right slope,70 m from the meteorological station	III	NE	Virgin land	Calcareous medium-deep clay-loamy chernozem
4	Same as above	III	NE	Virgin land	Same as above

* Soil sections are described in (7)

mean annual rainfall and only two events of "solid" runoff out of six rainfall events. Maximum total rainfall was observed in June and was as great as II9.7 mm. The rainfall intensity for two events of "solid" runoff (on June 7 and I4) varied from 0.I to 0.6 mm/min. It was the first shower on June 7 that determined the subsequent behavior of the pesticide.

Results of BHC behavior modeling and field measurements for plots No.I (fallow) and No.2 (kidney beans) are shown in Fig.I and 2. Curves b,c,d and e in Fig.2 were obtained using the values of degradation rate that correspond to the contributions of various processes to degradation given in Table 3.

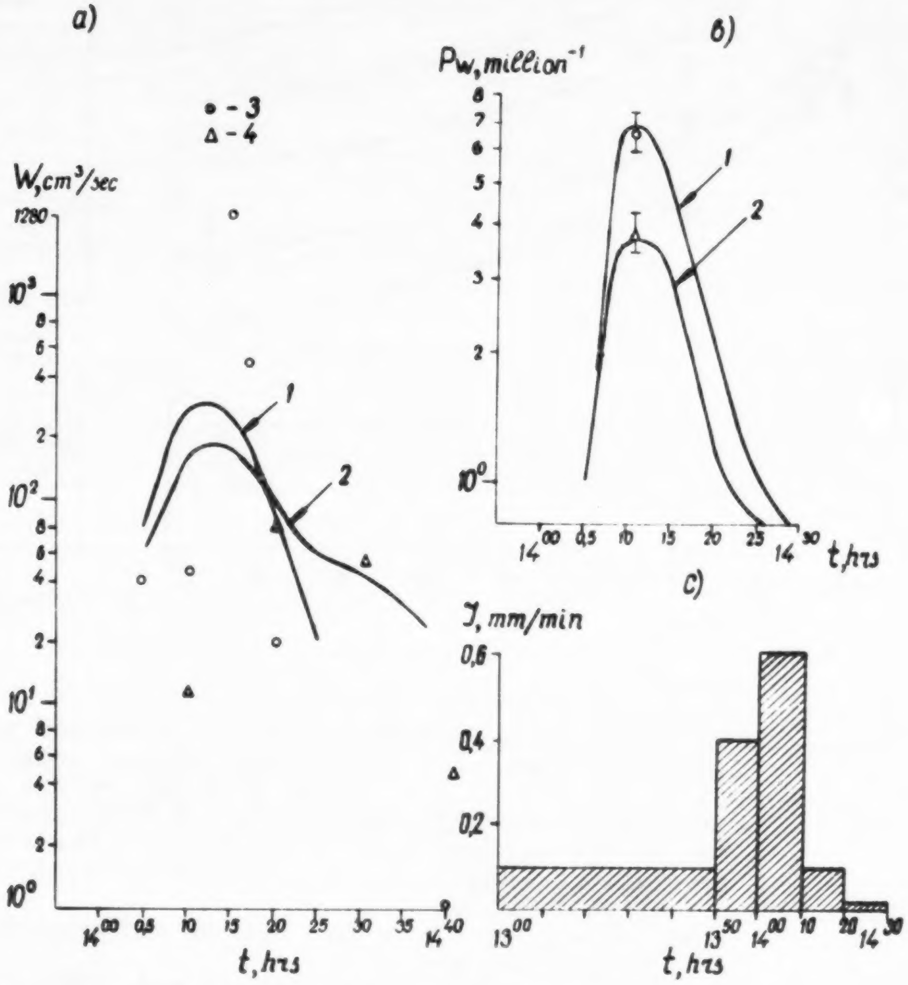

Fig.I. Calculated using the model (I-kidney beans, 2 -fallow) and measured (3 - kidney beans, 4 - fallow) water discharges and BHC concentrations in the sorbed state on suspended sediments during the first shower on June 7, I980: a) water discharges; b)BHC concentration in"solid"runoff; c) rainfall intensity.

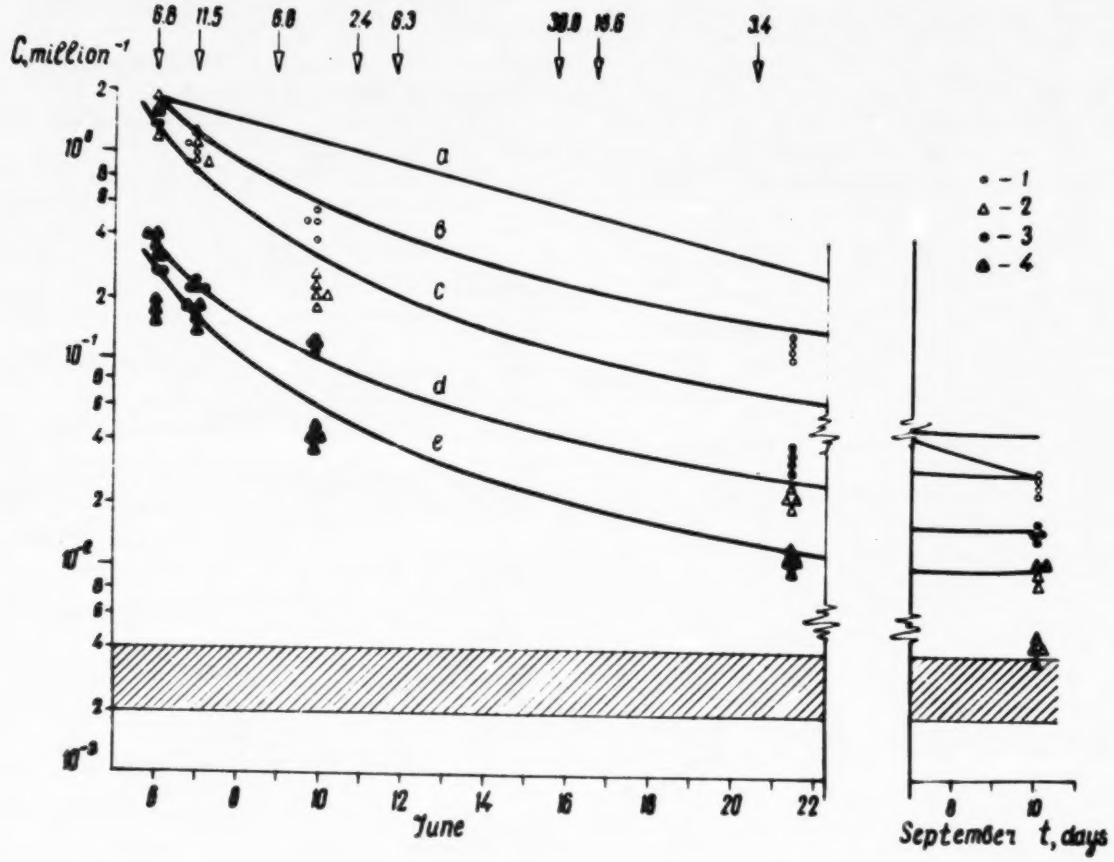

Fig.2. Calculated using the model (a,b,c,d,e) and measured (I,2- α - isomer for fallow and kidney beans, respectively; 3,4 - γ - isomer for fallow and kidney beans, respectively) variations of BHC concentration in the surface zone for two plots(Moldavia):

a - sum of isomers at a constant rate of degradation;
b and c - α - isomer for fallow and kidney beans, respectively;
d and e - γ -isomer for fallow and kidney beans, respectively.

Arrows denote the daily rainfall layers and a cross-hatched area shows the background values.

Analytical determination of BHC residues was performed by gas-liquid chromatography in accordance with the technique described in (8). BHC concentrations in the surface zone of the plot with kidney beans were somewhat lower than in the fallow plot at the same rate of BHC application. This was likely to be associated with larger water discharges in the plot with kidney beans during the shower on June 7, as well as with the entry of a part of BHC into the plants.

To study more thoroughly the vertical migration of labelled BHC in soil, field experiments were carried out on small plots at the Valdai station for water-balance investigation, beginning on September 22,I979. Monoliths were sampled in the experimental plots with clover where ^{36}Cl- and ^{I4}C-labelled BHC was applied, and the activity of chlorine-36 and carbon-I4 was measured in the soil layer-by-layer(I cm apart). Results of the measurements showing the vertical distribution of BHC in the soil layers, and the distribution of ^{36}Cl and ^{I4}C between the mineral part of the soil and plant residues for three seasons (winter, spring and summer) are given in Fig.3. The content of BHC in each layer is given in percent of the total content at the time of measurement. The results are indicative of a very slow movement of BHC through the soil profile. Three months after its application almost the whole of BHC (over 90% of its total amount in the soil) was found in the upper I cm layer and aerial portions of plants,probably, due to a mechanical pollution of plants, when applying the pesticide. Even at a depth of 3-4 cm only traces of BHC were detected. During the second sampling period (May I980),i.e. after the spring snow melt, BHC was found at a depth of 5-6 cm,however its greater part was localized in the upper two centimeters of the soil. A year after the application,i.e. in September I980, the greater part of BHC was found in the upper three centimeters of the soil profile. As to the mechanism of vertical movement of BHC, one can suggest the following: a strong sorption of BHC by the soil, especially by its organic part, is almost irreversible(desorption is no more than I0%). An insignificant depth of BHC migration enables one to suggest that the vertical transport of BHC through the soil profile occurs on fine soil particles which carry BHC in the sorbed form. Agreement between the characteristic dimensions of the vertical transport of BHC and that of the fine particles (I0) is also indicative of this fact. The ARM model does not describe slight movements of this kind,therefore estimated characteristic scales of the vertical migration do not exceed the depth of the surface zone(about I cm).

Based on the presented preliminary results we can conclude that:

- the model permits to carry out field experiments in various soil-climatic zones of the country;
- the model as a whole describes adequately the behavior of pesticides in a watershed .

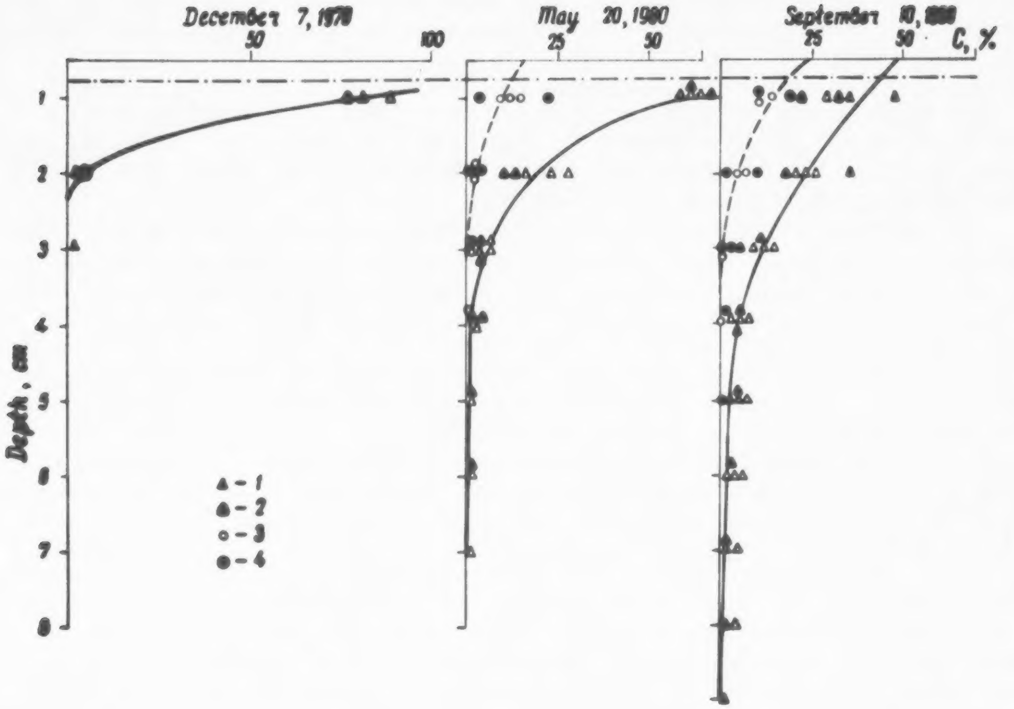

Fig.3. Dynamics of the vertical migration of BHC due to the transport of fine particles carrying it in the sorbed state(Valdai,1979-1980). Solid lines denote the measured profiles of mean concentration in soil(1,2-^{14}C- and ^{36}Cl-labelled BHC,respectively); dashed lines - those in plant residues(3,4-^{14}C-and ^{36}Cl-labelled BHC,respectively); and dash-and-dot lines - the data calculated using the model.

The latter conclusion,however,should be confirmed in further experiments on various pesticides and larger areas. The problems arousing in this case are associated with a spatial inhomogeneity of watersheds,as well as with inhomogeneity of rainfall and pesticide application. Attention should be given to limitations of the model, such as the assumption on equilibrium sorption and instantaneous dissolution,that may affect substantially the accuracy of prediction. However,primary attention should be given to degradation rate constant which is presently thought as a parametric description of the processes of evaporation and chemical and microbiological transformation. So far there is no methods for predicting this rate constant. It is necessary to describe differentially all these processes and find relations between the parameters of the processes and environmental parameters.

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EMPIRICAL PREDICTION OF SPACE REDISTRIBUTION OF POLLUTANTS IN SOIL ON THE BASIS OF FIELD TESTS

by

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There are varipus ways to solve the problem of predicting the behaviour of a substance in soils. Along with the prediction based on physical-mathematical modeling, it is possible in some cases to provide a long-term prediction of substance behavior in a soil-plant cover on a purely empirical basis by way of studying the major processes of migration and transformation under field conditions.

This paper presents approaches and methods for obtaining such a prediction.

It has been known a great variety of processes of substance transformation and migration as to their nature, intensity and direction, occur in soils. For the purposes of prediction it is necessary to know a number of parameters that could characterize to an adequate accuracy these major processes and their variation depending on soil-climatic, meteorological and other conditions. Inasmuch as even, the major processes for any substance in soil are numerous and diversified in their nature and a great body of data is required for prediction, it is advisable that the most productive and informative methods of full-scale observations be used to obtain the data. A method of isotope indicators that enables one to carry out direct observations and characterize the processes quantitatively meets this requirement to the greatest extent.

We consider briefly the main parameters required for prediction, using as an example two substances with different behavior in soil -BHC and zinc in ionic form. To perform predictive calculations, the following data should be available:

I. Quantitative relationship between various forms, groups and fractions of a substance in soil that differ from each other in migration capacity, availability for plants, stability to degradation factors, etc. The groups can be represented by substances sorbed by moving fine fractions of soil associated with humus substances that entered plant biomass and reentered the soil with plant residues, etc. For example, for BHC its division into two forms, i.e. the initial substance and the substance changed to a sorbed state is sufficient.

BHC can partly be in the initial state for a long time. The rate of its change to the sorbed state is limited not by the kinetics of sorption from solutions as thought sometimes but by the kinetics of its dissolving in a soil solution. On surface application in May, up to 30 per cent of BHC left by late September can remain in the initial nonsorbed state. Migration and in particular,degradation and evaporation of these forms of the substance will occur differently, and therefore predicting the transformation of the initial form of the substance is an important condition of the migration prediction.

Unlike BHC, zinc requires even more fractional differentiation, at least by 4 forms: I) exchange-sorbed zinc;, 2) zinc that reentered the soil with plant residues; 3) zinc associated with humus substances; and 4) fixed zinc remaining in the soil after separation of the three previous forms.

2. Migration capacity R_F of various forms of a substance with respect to migration capacity of water taken as unity. This parameter is used to estimate the mean downward movement of a substance in the soil over the seasons. For example, in sandy soddy-podzolic soils the value R_F amounted to 0.008-0.0I3 for BHC and 0.006-0.07 for various forms of zinc.

It should be noted that migration capacity R_F of a dissolved substance is determined by its sorption characteristics in a given soil, and in particular, by sorption isotherm.Thus, this parameter includes implicitly sorption and other factors of movement for a moisture nonsaturated soil and directed flow of soil moisture.

As a substance sorbed on a fine soil material moves, R_F characterizes the movement of this material itself which is a carrier of the sorbed substance.

3. Nature of redistribution of individual forms in various soil horizons in the process of migration. While the parameter R_F characterizes the mean movement of a substance, in this case we consider the form of vertical distribution curve of a substance in the process of its migration.

The nature of distribution for zinc, BHC and some other substances in sandy soddy-podzolic soil was determined only by the value of the mean movement of a substance. The curves obtained experimentally enable one to perform a layer-by-layer calculation of substance redistribution at its various mean movements in soil and any initial distribution. The calculation is based on the following assumption: the substance movement of the ith layer is independent of that of any other layer. This is obviously true for the linear portion of sorption isotherm.

4. Mean movement and distribution of various forms of a substance over the surface under the influence of surface runoff in individual seasons. Required experimental data are obtained and subsequent calculations performed in much the same way as the calculation of the vertical redistribution of

a substance. On surface movement,however, one observes a very wide-range variation depending on the erosion processes.

5. Plant root uptake by plants of various forms of a substance localized at different depths(coefficients of uptake from various soil layers). Based on these data and the information on substance distribution between roots and aerial portions of plants,we predict its movement in the soil as a part of the living phase,i.e. downward movement of the substance entered the biomass of plants with growing roots and its translocation to the surface with areal portions.

For metals that entered the soil surface covered with grasses this can be a major route of substance transformation and movement. For example, when entering the soil in early spring, up to 80 percent of ion Zn^{2+} is incorporated in the biomass by the end of the growing season and migrates to a considerable depth with growing roots(Fig.I). This route plays a minor role for BHC,though in some cases it can be incorporated in the biomass of vegetating plants by IO per cent or over.

6. Sunbstance losses from the aerial portions of plants in the process of transpiration. Experimental estimation of this route for BHC showed that it can be neglected in prediction calculations.

7. Effective substance losses from various layers of soil by evaporation, biodegradation and chemical degradation in various seasons.

It should be remembered that the rate of effective losses is determined largely by the incorporation of pollutants in various components of soil. In particular,BHC applied to the soil as a dust was "lost" several times more rapidly than the same substance sorbed by fine fractions of the soil. Consequently, a necessity arises for a differential determination of the rates of net effective losses for various forms of a substance transformed in the soil(Table I).

Table I

Approximated values of BHC half-life (days) in sandy soddy-podzolic soils covered with permanent grasses

Period of observation	At the surface		At the depth of IO cm	
	"free"	sorbed	"free"	sorbed
Spring (March IO-May 5)	50-70	I20-I50	-	200
Summer (May I5-Sept.20)	20-30	I20-I50	50-70	200
Autumn (Sept.20-Dec.I)	60-70	250	70-80	400

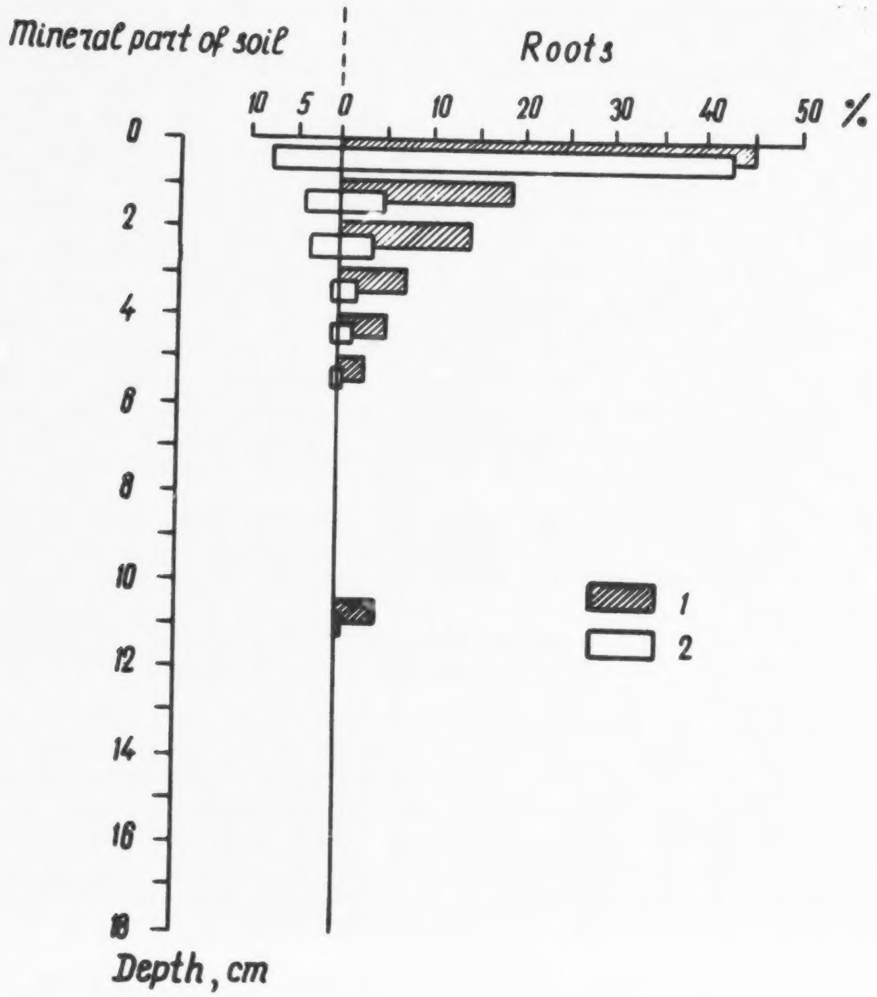

Fig.I. Vertical downward movement of zinc as a part of herb roots: I - the root biomass and 2 - the content of zinc. Rectangles at a level of II cm show the total amount of zinc in the 7-I8 cm layer.

It is advisable to perform prediction calculations for the soils of taiga region of the Soviet Union in succession over the three seasons of the year.

Winter-spring period lasts from a stable soil freezing (or from the time when negative temperatures begin to prevail) to a complete disappearance of melt waters. In this period, an intensive abiogenic transport of a substance with moisture flows is observed, and in the case of complete soil freezing the substance movement over the surface with surface runoff can prevail.

Summer period lasts throughout an active vegetative season of plants. In this period there occur an active biological uptake and redistribution of a substance through the soil profile, its biotransformation, biodegradation, losses by evaporation, etc.

Autumn period lasts from the end of the active vegetative season of plants to the beginning of the winter-spring period. As a rule, the most intensive downward movement of a substance through the soil profile is observed in this period.

Prediction calculations are performed by stages from one period to another, with a substance distribution through the soil profile over any period being an initial one for its redistribution calculation over the next period.

Fig.2 shows experimental (over the initial period) and calculated distribution in the soil of BHC surface-applied in September I979 over a period of 3 years (to September I982). Experimental tests conducted in May and September I98I showed that the character of distribution and the depth of penetration can be predicted fairly accurately. The largest discrepancies(about 50%) are related to the estimation of the total amount of BHC in the soil. The actual losses by evaporation and degradation occur slower that appears to be associated with an increasing stability of BHC, as it is present in the soil for a long time. It is apparent that further refinement of the degradation parameters is required.

The behavior of zinc can be predicted more accurately (Fig.3). A biological factor is the major one in the profile redistribution as soon as zinc entered the soil surface under study in the form of $ZnCl_2$. This is associated with the localization of the substance in the most active root zone. Four months after the entry, over 80 percent of zinc was incorporated in the biomass of plants, with 30 percent being redeposited at the surface as dead residues whereas most of the rest substance was distributed through the soil profile in accordance with the distribution of the root system. By the beginning of the autumn migration period the major portion of zinc was transformed to organozinc compounds of plant residues most capable of migration. This process had a pronounced effect on the further behavior and distribution of zinc through the profile.

As a result of abiogenic migration, a considerable part of zinc was found to be beyond the limits of localization of the major portion of active roots (the upper 3 cm of soil) even in the first autumn period. This movement resulted in: I) sharp decrease in the biological uptake of zinc in the subsequent periods; 2) sharp decrease in the rates of total downward migration as a result of decreasing biological producing of zinc forms most capable of migration; 3) progressive decrease of zinc washout by spring waters with surface runoff.

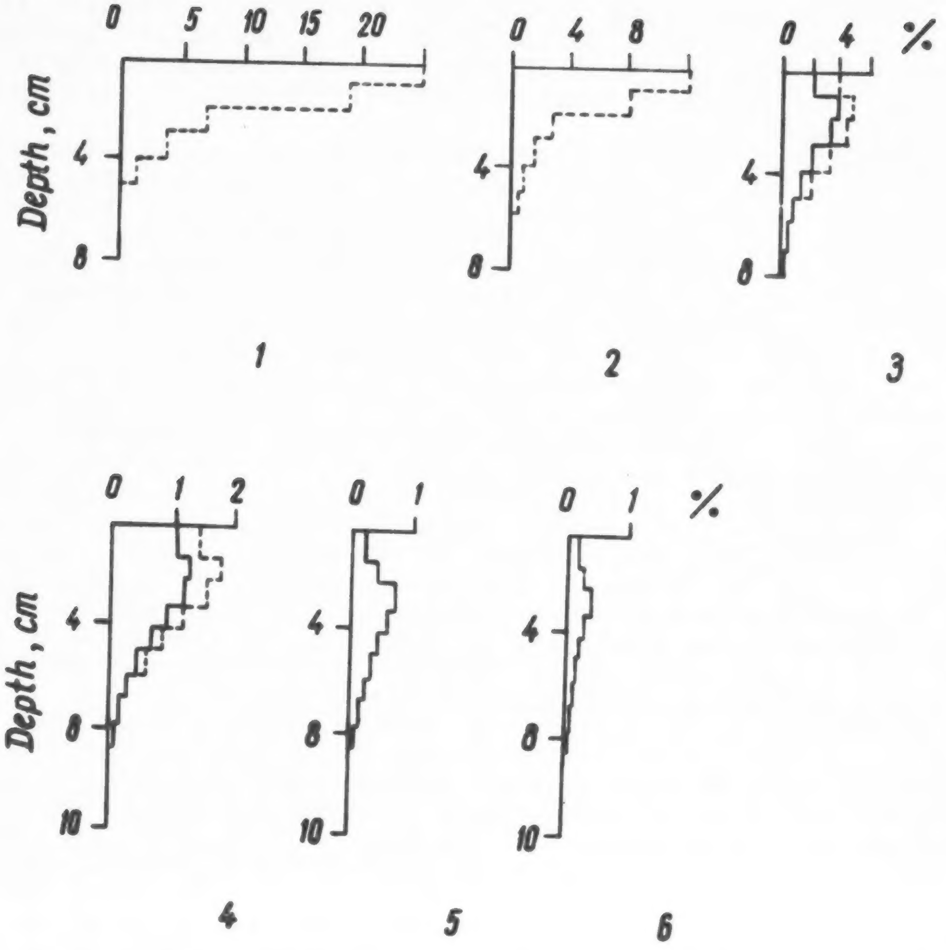

Fig.2. Experimental (dashed lines) and predicted (solid lines) redistribution of BHC in the soil:
I-6 denote May I980, September I980, May I98I, September I98I, May I982 and September I982,respectively

Approximately 2-4 years after the application, the biological factor ceases to be dominant due to the fact that the major part of zinc is now beyond the area of main root uptake, and the general migration is determined mainly by abiogenic factors of the movement.

During 3-4 years after the entry of zinc into the soil the average effective rate of downward migration decreases from 3 cm per year to 0.6 cm per year and is practically

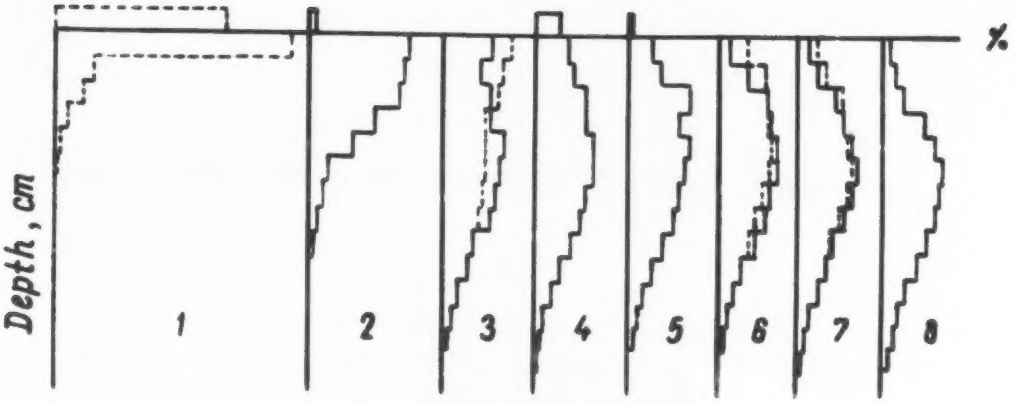

Fig.3. Prediction of zinc redistribution in the soil(solid lines).Experimental data are shown as a dashed line.
I-8 denote September I978, December I978, May I979, October I979, December I979, May I980, May I98I and May I982,respectively.

stabilized. This enables one to estimate to a first approximation the time of "clearing" the 30-cm soil layer by 50 percent which is about 30 years(for a single application).

Testing the suggested empirical model for zinc for two years showed a satisfactory agreement between the experimental and calculated data.

PREDICTING THE BEHAVIOR OF PESTICIDES IN SOIL

by

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Predicting the consequences of pesticide use makes it possible to regulate most efficiently the selection of pesticides to be used and their application conditions (application rate, frequency of treatments, alternation of chemicals,etc), as well as the choice of crops to be treated, with regard to climatic and geographical factors,etc. This approach permits to protect the environment effectively even before a new pesticide is brought into use or the area of application of the pesticides already used is broadened(7). This relates primarily to soil which is the site of maximum accumulation of persistent pesticides and the most important link of substance migration in ecological chains of the biosphere.

One way of solving the problem is mathematical modeling of complex systems, among which is a pesticide-soil subsystem. The work in this area is being carried out in three directions.

I. The first direction is synthesis of a mathematical model of pesticide destruction in soil from field data. The most universally employed is modeling the process of pesticide destruction in soil using the expression

$$C(t) = C_0 e^{-\frac{t}{T}}. \qquad [I]$$

Experience suggests,however,that such an expression permits the values of concentration C(t) to be predicted fairly accurately for short periods of time only.

Therefore it would be possible to use a more complex expression

$$C(t) = \sum_{i=1}^{n} C_i e^{-P_i t}, \qquad [2]$$

where constants C_i satisfy the following condition:

$$\sum_{i=1}^{n} C_i = C_0 \,. \qquad [3]$$

However, evaluating the corresponding parameters is a very complex problem.

It is known(3) that the expression

$$C(t) = C_0 e^{-\frac{t}{T}} \sum_{i=1}^{n} \frac{\left(\frac{t}{T}\right)^{i-1}}{(i-1)!} \,. \qquad [4]$$

is more appropriate for long-term prediction that [2] .

To assess effectively parameters C_0, T and n we worked out an algorithm of self-organization. The main point of this method (I) is as follows: two sequences-learning and checking are chosen from the set of initial data. The learning sequence is used to optimize the parameters of the polynomial which models the process, and the checking sequence to choose a degree of the polynomial. Optimization of parameters in the learning sequence is performed as in a conventional analysis of regression, whereas in the checking sequence a regularity criterion is used for this purpose.

We shall determine an optimum structure of [4] for the process of dipterex(chlorofos) destruction in soil. Experimental data are presented in Table I. We choose any three experimental values as learning sequence and the entire series as checking sequence. This procedure enables us to perform optimization over four points only. Assume that a value

$$\delta_i = 100 \frac{\sum_t \left[C(t) - C_n(t)\right]^2}{\sum_t \left[C(t) - \hat{C}\right]}, \quad i = 1,2 \qquad [5]$$

is the regularity criterion (δ_1) if summation is over all points, and the optimization criterion (δ_2) in the learning sequence if summation is over three points. In formula [5] , $C_n(t)$ is the calculated value of pesticide concentration at a corresponding value n, C(t) is the experimental values, and $\hat{C} = \frac{1}{4} \sum_t C(t)$.

It is necessary to specify an interval of permissible values T. In this example T was assumed to range from 2 to 40 days. Step of change in T was 24 hours.

Table 2 presents calculation results when the first three points were chosen as learning sequence. It is seen from Table 2 that both δ_1 and δ_2 reach their minima, as n increases, but these minima do not coincide. The optimum value of n

Table I. The process of chlorofos destruction in chernozem (field studies)

t, days	3	I2	27	46
C(t),mg/kg	2.I3	I.59	0.84	0.03

should be chosen by criterion δ_1 , as it has the properties of external addition, whereas δ_2 is the internal criterion and reaches its extreme only due to a specific character of expression [4] . In addition to this, δ_1 characterizes directly the accuracy of approximation over all points. To establish the dependence of model selection on sampling division we determined optimal values of n for all four possible versions. The results indicate that irrespective of the division, one and the same model structure is selected by criterion δ_1 (n = 3). Position of the δ_2 extreme ranges from n = 2 to 5. Note also that criterion δ_1 reached its deepest minimum when the point of the initial data that was latest in time had been included into the checking sequence.

Table 2. The process of model structure optimization

n	I	2	3	4	5	6
T	27	I3	8	6	5	4
δ_1	6,8	2,7	I,72	2.4	3.I	4.2
δ_2	0.38	0.29	2.I7	4.3	5.8	8.3
C_0	2.4	2.I5	2.I4	2.04	I.98	I.98

Thus,to model the process of dipterex destruction, it is advisable to use the following expression:

$$C_3 = 2.I4\,(I + t/8 + t^2/I28)\,e^{-t/8} \quad . \qquad [6]$$

Calculations with formula [6] are much more accurate than those with [1] that is seen from Table 2, where the case n = I corresponds to a simple exponential function [I] .

Similar methodology can be used to work out a new approach for describing biocide destruction in the pesticide-soil-plant system. In this case, unlike the previous example, we set ourselves a task of determining the parameters of expression [4] in terms of physical-chemical and biological properties of the modeled system. Synthesis of the model is performed using the algorithm of the group method of data handling (GMDH) (2). For this purpose we can use the initial data obtained under field conditions(Table 3).

Vector of input variables X consists of four groups of factors:

I) properties of chemical: X_I - molecular mass; X_2 - solubility in fats; X_3 - melting temperature; X_4 - persistence at pH = 5 to 8 ; X_5 - persistence at pH < 5; X_6 - persistence at pH > 8 ; X_7 - solubility in water; X_8 - volatility;

2) properties of plant (percentage composition): X_9 - water; X_{IO} - nitrogen-free substances; X_{II} - fats; X_{I2} - cellulose; X_{I3} - ash; X_{I4} - sugar; X_{I5} - albumin; X_{I6} - protein;

3) properties of soil: X_{I7} - pH of salt (water) extract; X_{I8} - hydrolytic acidity; X_{I9} - humus content, % ; X_{20} - machanical composition; X_{2I} - total absorbed bases; X_{22} - content of P_2O_5, mg/kg ; X_{23} - content of K_2O, mg/kg; X_{24} - volume weight;

4) application conditions of chemical: X_{25} - application rate,kg/hectare; X_{26} - frequency of treatments; X_{27} - average temperature, °C ; X_{28} - average moisture,% ; X_{29} - total rainfall, mm; X_{30} - degree of plant coverage of soil (on the three-point system).

Of I6 realizations, I2 are used for self-organization of the model by the algorithm (2), and the rest (the last four in Table 3) constitute the checking sequence intended for a final choice of an optimum model among several models of equal value. An accuracy in the checking sequence serves as optimality criterion.

Modeling algorithm has two levels:

- self-organization for each experimental curve of degradation;
- synthesis of the polynomial dependences of chain parameters (n , T, C_o) on the vector of input variables $\bar{X} = \{X_9 \ldots X_{30}\}$.

Modeling results indicate that all curves of dipterex degradation can be given with an adequate accuracy by polynomial (4) at n = 2.

Thus, we set ourselves a task of self-organizing the mathematical models for T and C_o. This stage is the most important, since the models obtained are expected to be used as a basis for synthesis of a comprehensive model of the process of pesticide destruction.

The process of self-organization of the model of the dipterex-soil-plant system consists of two stages: I) self-organization of equations; and 2) test of their workability. Instead of [5] , we use the following formula:

Table 3. Initial data for modeling the chlorofos-soil system

Input variables								
9	I0	II	I2	I3	I4	I5	I6	I7
77	43.8	2.6	26.6	7.4	7.2	I3	I8	6.5
77	43.8	2.6	26.6	7.4	7.2	I3	I8	6.8
76.3	84.2	0.45	3.5	4.9	I	2	7	6.05
76.3	84.2	0.45	3.5	4.9	I	2	7	6.3
59	46.3	3	29.I	7.3	6.9	I0	I3.4	6.3
78	44.8	3.2	20.5	I3.6	7.7	9	II.3	5.4
78	44.8	3.2	20.5	I3.6	7.7	9	II.3	5.4
78	44.8	3.2	20.5	I3.6	7.7	9	II.3	5.3
78	44.8	3.2	20.5	I3.6	7.7	9	II.3	5.3
59	46.3	3	29.I	7.3	6.9	I0	I3.4	5.3
93.5	0.95	0.2	0.9	0.5	2.7	0.6	0.I	5.7
93.5	0.95	0.2	0.9	0.5	2.7	0.6	0.I	6.2
78	44.8	3.2	20.5	I3.6	7.7	9	II.3	5.4
76.3	43.9	3	26.3	9.9	4.7	I5.3	20.3	6.7
8I	8I.7	I.7	I2.3	22.3	I2.7	9.5	II.9	5.2
90	53.9	2.8	0.8	0.7	4	I.7	0.3	5.5

Table 3. (continued)

Input variables								
I8	I9	20	2I	22	23	24	25	26
I.4	3.9	30	27.8	II5	I20	I	2	I
I.7	4.6	40	26.8	II5	I20	I.06	2	I
I.53	3.48	30	2I.2	86	4I	I.I9	3	I
I.82	3.9	20	27	I89	80	I.09	3	I
I.82	3.9	20	27	I89	80	I.09	3	I
4.2	3.2	25	7I	I00	80	2.63	I.2	I
4.2	3.2	25	7I	I00	80	2.63	I.2	I
4	3.I	I5	70	50	80	2.62	0.9	I
4	3.I	I5	70	50	80	2.62	I.2	I
4	3.I	I5	70	50	80	2.62	I.5	I
I.98	4.9	20	32	I39	220	I.2	I.75	I
2.46	4.9	20	30.2	I40	230	I.2	I.75	I
4.2	3.2	25	7I	I00	80	2.63	0.6	I
I.8	5.52	40	27.8	9I	II8.7	I.I	I.75	I
2.46	4.9	20	29	I25	I34	I.2	I.75	I
2.46	4.9	20	48	44	72	I.2	I.75	I

Table 3 (continued)

Input variables				C_o	$\tilde{C}_o$	T	$\tilde{T}$
27	28	29	30				
I7	74.6	628	2	0.I2	0.II4	I2	II.02
I2.3	74	I94.I	2	0.3	0.306	I3	I2.92
I5.I	79.7	347.I	I	0.63	0.6	3	2.27
I7.I	74.6	264	I	0.I4	0.I5	I9	I8.93
I7.I	74.6	264	2	0.I3	0.I7	I7	I7.44
I9	77	36.I	I	0.I5	0.I3	4	3.88
I6.5	80	39	I	0.22	0.I8	3	3.64
I7.I	70	33.I	I	0.I9	0.I9	I	0.976
I7.2	72	22.I	2	0.I8	0.I8I	5	5.II
I7	67	53	I	0.4	0.4	3	3.05
I7.3	7I	246	I	0.3	0.254	3	3.52
I7.3	70	239	I	0.I	0.I4	5	5.03
I8	70	II8.5	I	0.98	0.7	I	0.74
2I.7	52	II5.3	2	0.2	0.28	II	II.4
I7.3	7I	246	2	0.I9	0.23	4	3.8
I7.2	69.6	237.I	I	0.II	0.I4	5	7.8

$$\delta = \frac{\sum_{i=1}^{N} (y_i - \tilde{y}_i)^2}{\sum_{i=1}^{N} (y_i - \bar{y})^2} \cdot 100 , \qquad [7]$$

where N is the number of observations; y_i is the experimental values of response (T or C_o) ; $\tilde{y}_i$ is the calculated values of response; $\bar{y}$ is the mean response.

We obtain the following expressions for T

$$T(\vec{x}) = -9.63 + 370.5 \; 1/x_{19} x_{28} + (28 - 3159 \; 1/x_{17} x_{21} + \qquad [8]$$

$$+4.9 \; x_{28}/x_{29} + 0.4 \; x_{13}/x_{30} - 0.8 \; x_{21}/x_{17}) \, x_{25}/x_{24} ,$$

and for C_o :

$$\tilde{C}_0 = x_{25} \sum_{i=0}^{9} a_i z_i \qquad [9]$$

(the values a_i and z_i are given in Table 4).

Table 4. Values of terms of the series in expression [9]

Term of the series No. (i)	Argument (z_i)	Coefficient(a_i)
0	I	-0.775
I	$I/X_{I7}X_{27}$	57.43
2	$z_I^2/X_{I9}X_{30}$	3135
3	X_{27}/X_{28}	0.383I
4	$z_3^2 \; X_{25}/X_{I7}$	2.I4I
5	$z_4^2 \; X_{25}^2$	-5.977
6	$z_I^2 \; z_4$	355I0
7	$z_5^2 X_{I9}/X_{30}$	-587.4
8	$z_8 X_{25}/X_{I9}$	0.I65I
9	$z_8/X_{24}X_{25}$	I.654

Corresponding calculated values of $\widetilde{T}$ and $\widetilde{C}_0$ are given in Table 3. The models obtained are resistant to variations of the initial data, as evidenced by a small value of error in the checking sequence.

Substitution of equations [8] and [9] in [4] gives a complete model of the dipterex-soil-plant system. The model permits predicting the degradation curve of a chemical at known values of input variables ($X_{I3}, X_{I7}, X_{I9}, X_{2I}, X_{24}, X_{25}, X_{27}, X_{28}, X_{29}, X_{30}$).

Synthesis of a comprehensive model of the dynamic pesticide-soil system is possible by self-organization of the third-level model based on the second-level dependences. In this case, an adequate quantity of experimental data should be available to assess coefficients of models [8] and [9] for a large number of pesticides. The third-level model is the dependences of the coefficients of expressions [8] and [9] on the physical-chemical properties of chemicals($X_I, \dots, X_8$). Such a model will enable one to choose a chemical with consideration for its properties and detoxicative potentialities of the medium, as well as to predict the behavior of new chemicals under various conditions.

2. The second direction is physical modeling of the process of pesticide destruction in soil under laboratory conditions. In this case, various methods of mathematical design of the experiment are used (5,6,8). A multi-factorial experiment enables one to bring the modeled conditions closer to natural ones.

The suggested approach was tested in experiments aimed at studying the process of destruction in soil of DDT, BHC, lindane, dilor (dihydroheptachlor), 2,4-D, phosphamide(dimethoate), etc. Methods of mathematical design of the experiment were chosen with regard to the set hygienic task and specific character of the object studied. In this work, we used the methods of complete factorial experiment of the type 2^n, dispersion diagrams, the method of fractional replicas and so called mixed plans. These latter seem to be most appropriate for the set task, since they permit carrying out experiments with both quantitative and qualitative factors present.

We shall consider the approach suggested, using as an example the study on the process of lindane degradation in soil. To carry out a 5-factor experiment we used a mixed plan on the basis of the complete factorial experiment of the type 2^n made coincident with Latin square of the side 4 (4).

As factors, we tested soil temperature, its moisture, presence of microorganisms in the soil, sample hermetization, and type of soil. The first four factors were varied at two levels. The fifth factor(soil type) included four varieties: grey forest, soddy-podzolic, meadow-gley and chernozemic soils.

In all, we carried out I6 experiments in three replicas with various combinations of the factors studied. Lindane residues were analyzed by gas-liquid chromatography using chromatograph "Tsvet-5". The experiment was carried out for 60 days.

Dynamics of lindane disappearance from the soil was approximated by an exponential function of the form [I] .

Based on the exponential, we calculated half-life of the chemical T_{50} which was considered a characteristic of the actual stability of lindane in the soil in each of I6 experiments(Table 5). Relative error in Table 5 was calculated with

Table 5. Comparison of actual and calculated data on lindane disappearance from soil

Experiment No.	Half-life, days		Relative error
	T_{50} act.	T_{50} calc.	
I	28.0	26.I	6.8
2	26.9	32.3	20.0
3	53.8	57.5	6.9
4	3I.8	28.5	I0.4
5	4I.2	44.I	7.0
6	26.9	23.5	I2.6
7	53.8	48.7	9.5
8	46.7	48.I	3.0
9	58.3	66.9	I4.8
I0	36.8	4I.7	I3.3
II	63.6	66.9	5.2
I2	26.9	20.3	24.5
I3	63.6	70.7	II.2
I4	58.3	49.3	I5.4
I5	4I.2	36.I	I2.4
I6	35.0	40.3	I5.I

the following formula:

$$\delta_{rel} = \frac{|T_{act} - T_{calc}|}{T_{act}} \cdot 100\ \%$$

Experimental results were processed by the method of regression analysis. The following equation was obtained:

$$y=43.3=7.1x_1+2.5x_3+4.7x_4-1.9x_1x_2-3.0x_1x_3-$$
$$-1.6x_1xy-7.1x_2x_4-2.5x_2x_3+6.9x_1x_2x_3+2.8x_1x_3x_4-2.7x_2x_3x_4 \quad [I0]$$

where y is the half-life in days; x_i is the values of factors in the standardized form (-I) or (+I).

Table 5 shows half-lives calculated by equation [I0] ($T_{50\ calc.}$) compared to actual half-lives($T_{50\ act.}$). $T_{act.}$ varied from 26.9 to 63.6 days and $T_{calc.}$ from 20.3 to 70.7 days. Relative error exceeded I5% in two cases only. Root-mean-square error was II.6%.

Taking into account independent assessments of regression coefficient and rather high accuracy of prediction, equation [I0] can be considered as a model of the process of lindane disappearance from soil.

Analysis of this model enables us to draw the following conclusion. Among the factors studied, temperature had the strongest influence which was inversely proportional to persistence of the chemical. As temperature increased from 4°C to 40°C, the half-life decreased by I4.2 days (the effect of this factor is equal to a doubled coefficient of term X_I). Next is sample hermetization. The half-life for a hermetized sample exceeded that for an open vessel by 9.4 days, all other factors being equal. The influence of microorganisms showed itself as a decrease in the half-life by 5 days, with soil sterilization increasing this index by 5 days. The influence of soil moisture proved to be invalid. It should be noted, however, that there was a noticeable interaction of this factor primarily with sample hermetization factor (term X_2X_4), as well as with temperature and the presence or absence of microorganisms (term $X_IX_2X_3$).

The influence of the fifth factor (type of soil) was determined by the method of one-factor dispersion analysis. A period during which lindane persisted in soddy-podzolic soil was the longest (in the average, $T_{50} = 55.2$ days); in chernozem it was somewhat shorter ($T_{50} = 46.5$ days); and in meadow-gley and grey forest soils much the same.

Results of the dispersion analysis indicate that the extent to which the type of soil influences the persistence of the chemical is, on average, 36% of the total influence.

Thus, by means of a designed experiment we can study and assess, quantitatively the extent to which not only one or another factor exerts its influence, but their various combinations as well. The data obtained are used to predict the behavior of pesticides under field conditions.

3. The third direction is hygienic regulation of pesticides in soil, since the extent to which it is polluted by

pesticides that are foreign to soil can be assessed only by comparison with their maximum permissible concentrations(MPC). Up to the present, MPC for about 30 pesticides in soil have been experimentally substantiated and approved by the USSR Ministry of Health. In all, the assortment/list/ of pesticides used in this country contains about 200 items. The data presented indicate that experimental hygienic regulation alone of pesticides in soil, as weel as in other environmental objects fails to keep pace with chemicalization of the national agriculture. Therefore the task has been set to work out a method for accelerated substantiation of permissible content of pesticides in soil.

To substantiate MPC in soil it is necessary to take into account the extent to which chemicals migrate from soil to adjacent media (air, water, foodstuffs) and criteria for the hygienic norms on the permissible amounts of the compounds under study in the same media. Taking into account this peculiarity, we performed multiple correlation analysis of pesticide MPC in soil and of three factors: permissible residual concentrations (PRC) in foodstuffs, MPC in water bodies and MPC in the air of working zone. The sampling included I8 chemicals for which MPC in soil had been experimentally substantiated. Multiple correlation coefficient $R = 0.73$ is indicative of a high degree of interrelation. The analysis showed, however, that the interrelation revealed is based upon a close paired correlation for PRC ($r = 0.72$), whereas for the other two norms the correlation coefficient was 0.0I and 0.28, respectively. This result indicates that critical concentrations in soil of almost all pesticides were determined from their translocation to plants.

Based on the above assumptions, the following equation was obtained:

$$y = 1.23 + 0.48 \lg x ,$$

where y is MPC in mg/kg of soil; x is PRC in mg/kg of vegetative food product.

Comparison of the experimentally substantiated norms with the values calculated by equation $\boxed{II}$ showed that of I8 calculated values I6 did not exceed double MPC, and only for dalapon and phosphamide/dimethoate/ the ratio of calculated values to MPC was 2.46 and 4.0I, respectively (Table 6). This permits equation $\boxed{II}$ to be recommended for calculated hygienic regulation of pesticides. The corresponding norm was called approximate permissible concentration (APC) of pesticides in soil.

It is recommended to establish APC in those cases where MPC of pesticides in soil have not been substantiated yet or when their experimental substantiation is not reasonable because of low persistence of a chemical in soil, its limited usage, etc.

Thus, at the stage of preventive control it is necessary to calculate the norm for a new pesticide and its lifetime in

Table 6.,MPC and APC of pesticides in soil (mg/kg)

Pesticide	MPC	APC	APC/MPC
BHC	I.00	0.88	0.88
- BHC	I.00	0.88	0.88
DDT	I.00	I.08	I.08
Carbofos/Malathion/	2.00	I.23	0.6I
Prometryne	0.50	0.74	I.48
Polychlorcamphene/Toxaphene/	0.50	0.74	I.48
Polychlorpinene	0.50	0.I0	0.20
Sevin	0.05	0.I0	2.00
Chlorofos/Dipterex/	0.50	0.74	I.48
Gardona	I.40	I.I8	0.84
Heptachlor	0.05	0.I0	2.00
Dilor/Dihydroheptachlor/	0.50	0.74	I.48
Kelthane	I.00	I.23	I.23
Zineb	I.80	I.I2	0.62
Dalapon	0.50	I.23	2.46
Metaphos / Methyl parathion/	0.I0	0.I0	I.00
Fozalon	0.50	0.88	I.76
Phosphamide/ Dimethoate/	0.30	I.23	4.0I

soil, and then, by comparing the calculated values, to assess the regulations proposed (application rate, etc.). Regulating the use of pesticides in agriculture will make it possible to prevent soil and foodstuff contamination by pesticide residues.

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BIOTIC RESPONSES TO PESTICIDE POLLUTION OF NATURAL ECOSYSTEMS (PREDICTION ASPECTS)

by

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The background level of environmental pollution and the state of the natural environment are observed through the use of a special observation system called monitoring (6). Monitoring implies not only the detection of the level of environmental pollution by persistent chemical compounds but the assessment of ecological effects of the detected levels as well. The USSR State Committee for Hydrometeorology and Control of Natural Environment is the institution responsible for coordination of activities in this sphere. Prediction of biotic responses to pesticide pollution is an essential part of predicting the behavior of toxicants in the biosphere,which is determined by three main factors: (I) alien nature of most pesticides for natural chemical compounds; (2) wide spectrum of their biocidal effects and purposeful introduction directly into the natural environment; (3) interrelations of natural processes with the result that the effect of a pesticide on a certain natural component involves a chain of alterations in other ecological components.

Prediction of the fate and migration of pesticides is incomplete unless their interaction with biological objects is taken into account. It is necessary first of all to consider the possibility of toxicant accumulation in plants and animals, bearing in mind that pesticide deposition,on the one hand,and its degradation and excretion from the organism,on the other, are two sides of the same problem. Even small residual amounts of pesticides may seriously affect the organism and the population as a whole. Thus, negative effects of pesticides on the propagation of wild birds and other classes of animals were identified through observations on persistent organochlorine insecticides in the environment. This is noteworthy,as back in the sixties it was widely believed that the portion of DDT in biota is insignificant compared to its total mass circulating in the biosphere and amounts to about one-thirtieth of its annual production,i.e. no more than I·IO^4 tons (II).

The interaction of a pesticide with abiotic components in the environment ends with its degradation, while any contact of living components with pesticides often proves to be only the beginning of a long chain of transformations and leads to further effects which sometimes show themselves long after pesticide degradation. For example,rapidly degrading but highly toxic pesticides may exert a prolong effect on pedobionts. Thus,it takes about two years to restore the population of soil-inhabiting collembola,exposed to DD (dichloropropane-dichloropropene) with a degradation period in soil of 30 days (9).

Indications of the character of pesticide effects and the sphere of their application enable one to identify in advance those biological objects which are potentially most susceptible to these effects.

As a rule, insecticides are toxic not only to vermins but to various invertebrates as well (5,9,IO). For example,carbophos (Malathion) in terrestrial ecosystems is especially hazardous to pollinator insects (which should not be exposed to this insecticide) and predaceous invertebrates - natural enemies of plant-eating insects. Malathion used against blood-sucking insects in their breeding places is highly toxic to mollusks inhabiting these places. Metathion (sumithion) reduces the total numbers and biomass of herb-layer and soil-inhabiting invertebrates, ground beetles and other ground Coleoptera. It is hazardous to chironomid larvae, oligochetes and other aquatic invertebrates. Chlorophos (dipterex) causes death of the most important soil-formers —earthworms, etc.

Therefore, when predicting the behaviour of an insecticide intended to reduce the numbers of destructive invertebrates, one should reveal possible side effects exerted by this insecticide on other animal species of the same taxonomic group, taking into account their role in the ecosystem and specific conditions of its application. The same procedure should be used to assess pesticides intended for other purposes. Rodenticides used for reducing the numbers of sousliks, field mice and other destructive rodents can be hazardous to hare-like. Herbicides can injure non-target plant species, and so forth.

Insecticides, herbicides and rodenticides can constitute a direct threat not only to invertebrates, plants and rodents, respectively, which is also true for other pesticides. The range of pesticide activity, the degree and duration of its manifestation determine largely the danger of side effects. For example,some carbamate insecticides are very hazardous to mammals (7). There are herbicides (triazines, DNOC, etc) which cause significant long-term changes in the composition and component interrelation of pedocenosis. Many organophosphorus insecticides are highly toxic to birds and hydrobionts. Lethal doses LD_{50} of actellic, baytex, iodophenphos and carbophos to birds are within rather low range (30-60 mg/kg) in comparison to that for mammals (225-I400 mg/kg) (8). In the Soviet Union carbophos, chlorophos and actellic residues in analitically detectable amounts are inadmissible in fishery water bodies, and maximum permissible concentration of methathion is 0.0004 mg/l. Some insecticides possess phytotoxic properties: carbamate sevin causes ovaries of trees to fall off; dipterex is harmful to some tree and shrub species, and so forth.

Consequently,predicting the behaviour of pesticides and after effects of their application should be based upon the data on their toxicity to various classes of living organisms irrespective of the direct purpose of these compounds.

Responses of natural populations to toxicants are determined largely by the mechanism of their action which is responsible for their neurotropic, gonadotropic, embryotropic or other effects. Therefore, it is important first of all to consider possible side effects of :neurotoxic compounds on the behavior of animals under natural conditions; gonadotoxic compounds on reproduction processes; embryotoxic compounds on the posterity embryonic development for several generations, and so forth.

Neurotropic pesticides affecting the behavior of animals are most hazardous during the important periods of their life, such as breeding. A set of relevant data is presented in the Review Information on the world literature (4). Changes in the response to danger, mother's calls, feed and disturbances in motor activity and calling play a significant role in the prey-predator relations. Insecticides reduce the alertness of small mammals with the result that they no longer hide from predators and sometimes become more active. Such changes in their behavior result in increased prey devouring,for example, by, birds of prey,which most often attack moving animals. Neurotoxicity of dieldrin causes death of birds since they cease feeding and starve rather than die of direct poisoning by this pesticide. Similar effects were also observed in the experiments on mammals. Herbicide 2,4-D is known to reduce the motor activity of some species of ground beetles, while organophosphorus insecticides increase it. A female brown shrike(Lanius cristatus)ceased feeding its fledglings whose behavior had changed under the effect of iodophenphos, and remained in the nest in daytime (the active feeding period). In this case the fledglings died from both the direct toxic effect and hunger.

Pesticides characterized by gonado- and embryotoxic effects are of particular importance for the fates of natural populations. The experiments on sevine, a compound with moderate toxicity and weak accumulative capacity,carried out in different landscape-geographical zones under natural conditions revealed these effects on various species of small mammals. No mass death of the animals such as bank vole (Clethrionomys glareolus), Pallas's pica (Ochotona pricei),and great gerbil

(Rhombomys opimus) was observed immediately after the trial use of this insecticide in their habitats. Later on,however, the number of males and females participating in population reproduction decreased as did their general fertility,and the number of cubs in the populations reduced as a result of destructive changes in reproductive organs and embryo resorption. Even after a single treatment of the habitats this effect became more and more acute from brood to brood (2,6).

It is evident from the foregoing that when predicting the behavior of pesticides,one should take into account not only the possibility of acute effects, but the results of chronic exposure as well. The latter manifests itself both in case of persistent compounds and repeatedly used less persistent ones, since along with a material cumulation of pesticides in tissues, there exists a physiological cumulation which determines the accumulation of the effects.

It is also important to foresee possible indirect effects of pesticide application on animal populations which have no direct contact with the pesticide. These effects may be of great importance for biogeocenoses (ecosystems) depending on environmental conditions (2).

The danger of a pesticide in the environment is determined by the nature of ecological relations between various populations and the reproductive abilities of individual species. By way of example, we consider sevin. Laboratory experiments revealed its strong insecticidal effect on Collembola, small insects actively participating in plant litter decomposition. However, quite an unexpected effect was observed under natural conditions: the numbers of Collembola was maintained at a low level only for about a month and then suddenly increased. This was due to their short life cycle and great dispersal ability as well as by the mass destruction by sevin of their enemies: spiders, predaceous mites and other invertebrates whose populations did not reproduce themselves for a long time (I). Similar processes are responsible for propagation outbreaks of the pests subjected to chemical destruction and sometimes, of those species that earlier have not caused serious damage.

A steady drop in the population numbers of certain species can adversely affect the adjacent populations. A drop in the numbers of molluscs led to a decrease in the numbers of water fowl feeding on them. Facts are known that the mass death of earthworms in the forests treated with insecticides resulted in a sharp decrease in the population of moles and other animals feeding on the earthworms (I).

The extent of indirect changes in the biogeocenosis is determined by the ecological significance of species exposed to a pesticide. This is best seen in isolated ecosystems,such as island, upland,etc. where possibilities of population migration are limited. Under these conditions,the impact of gonado- and embryotoxic pesticides excludes the possibility of self-fregulation of the population numbers. Similar experimental pesticidal impact on Pallas's pica, the most important trophic and topical link in the mountain-steppe plateau, caused not only a steady decrease in the numbers of these animals, but also the destruction of their empty burrows used by other warm-blooded animals (some species of birds and predatory mammals) and invertebrates. In this experiment, a disturbance in the chain of biogeocenotic processes gradually led to certain changes in phytocenosis and, therefore, in the animal habitat conditions (I,3). The experiments on this insecticide enabled one to develop the methods for ecological assessment of pesticide effects on the fauna, and prepare for consideration the prediction information which permits foreseeing its negative effects on terrestrial ecosystems. In the Soviet Union, sevin is not used in tundra, boreal coniferous and mixed forests, and steppe. What is more, the presence of its residues in foodstuffs is inadmissible.

It is necessary to take into account that side effects of pesticides show themselves against the background of the existing levels of pollution by combinations of chemical compounds of anthropogenic origin. Therefore, biota is exposed to the combined action of various substances which can mutually enhance or weaken the toxic effect.

Thus, predicting the behavior of pesticides in the biosphere should give an idea of the integrated effect of these substances, including biotic responses to environmental pollution, against the background of the interaction between various natural and anthropogenic factors. Revealing in detail the role played by individual factors requires relevant experiments in ecostats and under natural conditions, in which case the prediction assessment of pesticide side effects acquires a closed-cyclic character.

Since the integrated prediction of pesticide behavior in the biogeocenosis cannot be based on the examination of all its components, of great importance is the choice of the proper key species to serve as useful ecological indicators.

Human interference in the processes occurring in natural populations is not necessarily harmful to them. However, predicting should take into account the scale of possible disturbances of the dynamic equilibrium and their ecological significance.

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PROGRESS IN PREDICTING THE PROCESSES THAT DETERMINE PESTICIDE CONCENTRATIONS IN AQUATIC SYSTEM

by

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The impact of a chemical on an aquatic system is clearly related to its concentration in the environmental compartments of interest (e.g. water, sediment, biota). Consequently, considerable research has been devoted to developing methods for "forecasting" expected environmental concentrations (EEC) of organic pollutants.

One predictive approach requires the use of computerized models of systems envisioned as having input and output (e.g. flow and transformation). These models incorporate mathematical descriptions of transformation and transport pathways as subunits. In such models, the pathways (i.e. processes) are usually described by either kinetic or equilibrium equations depending on our understanding of the processes, their temporal scales and the environments of interest.

The process descriptions, in turn, incorporate characteristics of both the environment and the chemical. To the extent that these characteristics can be generalized, they potentially provide a basis for extrapolating environmental behavior from one chemical to another or from one environment to another. The benefit of being able to make such extrapolations is obvious and accounts for much of the interest by government agencies or by industries that must assess the behavior of large numbers of chemicals in many different environments.

The processes shown below are those that seem most often to be important and that have been most intensively studied for uncharged organic molecules such as pesticides.

Sediment Sorption
Volatilization
Microbial Transformation
Chemical Transformation
    Photolysis
    Hydrolysis

Sediment Sorption

Photolysis and volatilization are covered by others at this symposium and will not be discussed in detail here.

Both sorption and volatilization are partitioning phenomena driven by the fugacity difference in two phases. The equilibrium distribution is given by the ratios of fugacity capacities in the respective phases. The ratio of any two partition coefficients (air/water, sediment/water, biota/water) also is given by the ratio of fugacity capacities which ultimately can be related to the activity coefficients in the respective phases (1).

For uncharged molecules, sediment/water partition coefficients may be described by Equation 1:

$$K_{oc} = \frac{C_{organic}}{C_{water}} = \frac{a_{organic}\ \gamma_{water}}{a_{water}\ \gamma_{organic}} = \frac{\gamma_{water}}{\gamma_{organic}} \qquad (1)$$

where a and γ are the appropriate activity and activity coefficient (Raoult's law reference state in both phases), and C is the chemical's concentration in the respective phases ($K_{OC} = K_p$/organic content of sediment). Mackay and Karickhoff (2-4) have suggested that differences in K_{OC} for different chemicals are largely due to changes in γ_{water} with $\gamma_{organic}$ being relatively constant. This presumably accounts for good correlations observed between such parameters as the octanol/water partition coefficient, K_{OW} and the sediment/water partition coefficient, K_{OC}, and between K_{OW} and the bioconcentration factor, K_B. Mackay (2) has recently demonstrated the constancy of $\gamma_{organic}$ for a wide variety of compounds and has also shown that $\gamma_{organic}$ varies for highly polar compounds such as organic acids or for high molecular weight chlorinated compounds. The reasons for these deviation are unknown but presumably the acids associate in the organic phase and the chlorinated compounds form less and less ideal solutions in organic solvents as the molecular weight increases.

Attempts to relate water solubility, S_W, to the octanol/water partition coefficient (5) or soil sorption coefficient K_{OC} are well known, and reasonable correlations have been obtained with data from both solids and liquids. If the crystal lattice energy is taken into account (usually through a melting point correction), however, significant improvements can be made. These approaches are discussed in the work of Mackay (4), Karickhoff (3), Yalkowsky (6), and Hansch (5). At present, as Karickhoff has pointed out, K_{oc} can be computed through three independent approaches: from K_{ow}, from S_w and melting point, and from a fragment constant approach. For most pesticides of interest, these methods should give parameter estimates that are within a factor of two of experimental values. They also provide an approach for examining the reliability of measured values.

The difficulty of measuring Kow and Koc, especially when these numbers are large, has prompted considerable interest in the use of high pressure liquid chromatography (HPLC) (7,8). This approach is usually based on a calibration between K_{ow} and retention volume. It is perhaps worth noting that the HPLC approach is based on partitioning between solvent and an organic sorbent. Consequently, the changes in $\gamma_{organic}$ mentioned earlier can be expected to result in large errors if broad extrapolations are made.

As noted earlier, sorption is usually assumed to be an equilibrium process. Although this assumption is probably valid for many environmental problems, it is important to determine the conditions under which one may expect kinetic limitations. There is abundant evidence in the literature that isotherms may exhibit hysteresis, and Karickhoff (9) has suggested that the time required for equilibration in sediments is directly related to the magnitude of K_p. Other data, such as those illustrated by Figure 1, show that "irreversible" sorption may strongly influence the transformation of chemicals in some cases. These results clearly indicate the necessity of an extensive reappraisal of sediment sorption kinetics because every fast transformation pathway can potentially be rate limited by sorption/desorption.

Hydrolysis

Transformation by abiotic hydrolytic mechanisms is relatively well understood. Even the important problem of abiotic catalysis, however, has only recently been examined for aquatic systems. Solution of the Brønsted equations indicates that general acid-base catalysis by dissolved inorganics or humic materials is unlikely to be important, at least in natural waters (10). Indeed, little is known about other catalysis mechanisms such as those involving metals or free enzymes or even about the kinetics of other chemical transformation pathways especially in sediment-water systems.

It is often tacitly assumed that sediments will catalyze chemical reactions or retard them due to sorption. For reactions in suspended sediments, however, there is little or no convincing evidence to support these contentions. There are several reasons for the lack of such data. First, the experiments are difficult to perform in a manner that guarantees sterility without compromising the chemical composition of the system. Second, precise quantitation is difficult in sediment systems, and it is not straightforward to account for the effects of sorption. Finally, observation of catalytic effects requires pH control, long reaction times, and competitive pathways must be slower. These conditions are difficult to attain while maintaining precision at low concentrations.

Some results from our laboratory illustrate the need for better understanding of the role of sediments. Table 1 shows the influence of sediment sorption on hydrolysis of hexachlorocyclopentadiene (Hex) (11). This compound is believed to react by an $S_{N}2'$ mechanism that is pH independent in water (Equation 2 where $[Hex]_T$ is the total amount of Hex per unit volume of water).

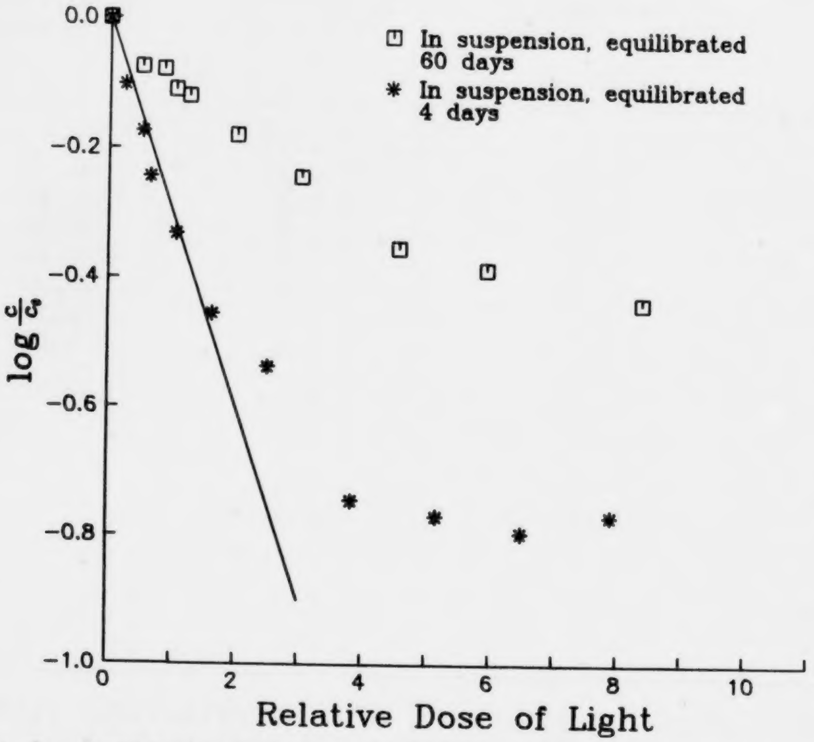

Figure 1. Comparison of kinetic data for photolysis of DDE under various conditions in suspensions of Mississippi River sediments.

$$\text{rate} = -\frac{d[\text{Hex}]_T}{dt} = k[\text{Hex}]_T \qquad (2)$$

If sorption is a rapid, passive equilibrium condition, the rate equation should be

$$\text{rate} = -\frac{d[\text{Hex}]_T}{dt} = \frac{k[\text{Hex}]_T}{1 + \rho K_p} = k'[\text{Hex}]_T \qquad (3)$$

where ρ is the amount of sediment per unit volume of suspension and K_p is the sediment/water partition coefficient for Hex. It is clear from the data that this reaction is not retarded as expected and is almost independent of the extent of sorption. The explanation for this behavior is unclear, but certainly there is no evidence of catalysis.

Table 1. Decay Rate Constants for Hex in Sediment-Water Systems.

Sample	Sediment Concentration g/100 ml	Decay Rate Constant $k, sec^{-1}, \times 10^6$	Fraction in Solution x/T[a]
EPA-13[b]	0.0	1.5 ± 0.6[d]	1
	0.05	3.5 ± 0.4	0.79
	0.10	4.4 ± 0.3	0.65
	0.15	4.5 ± 0.5	0.55
	0.20	3.7 ± 0.4	0.48
	0.40	2.7 ± 0.3	0.32
	1.0	3.4 ± 0.3	0.16
	2.0	2.1 ± 0.4	0.08
Oconee River(GA)	1.0[c]	1.78 ± 0.09	
	1.0	1.5 ± 0.2	
USDA (pond, GA)	1.0[c]	1.8 ± 0.3	
	1.0	2.0 ± 0.2	
Hickory Hills (pond, GA)	1.0[c]	3.4 ± 0.7	
	1.0	5.4 ± 0.7	

[a] The fraction of hex in solution (x/T) was calculated using a value of K_p obtained by the relationship between K_p and K_{ow} as described by Hassett et al. (14). [b] Organic content of the sediment is 3.0%. [c] Sterile systems. [d] Average value from Table 1.

The 2,4-D n-octyl ester behavior shown in Figure 2 illustrates rate limitation by sorption when "pH jump" experiments are carried out in hydrolyzing this compound (12). Figure 2 can be explained by rapid hydrolysis of the ester in the aqueous phase and rate limiting desorption from the sediment. This again emphasizes the necessity for thoroughly understanding sorption kinetics. We have also observed a similar kinetic limitation that was caused by wall adsorption when studying this compound in water alone (13).

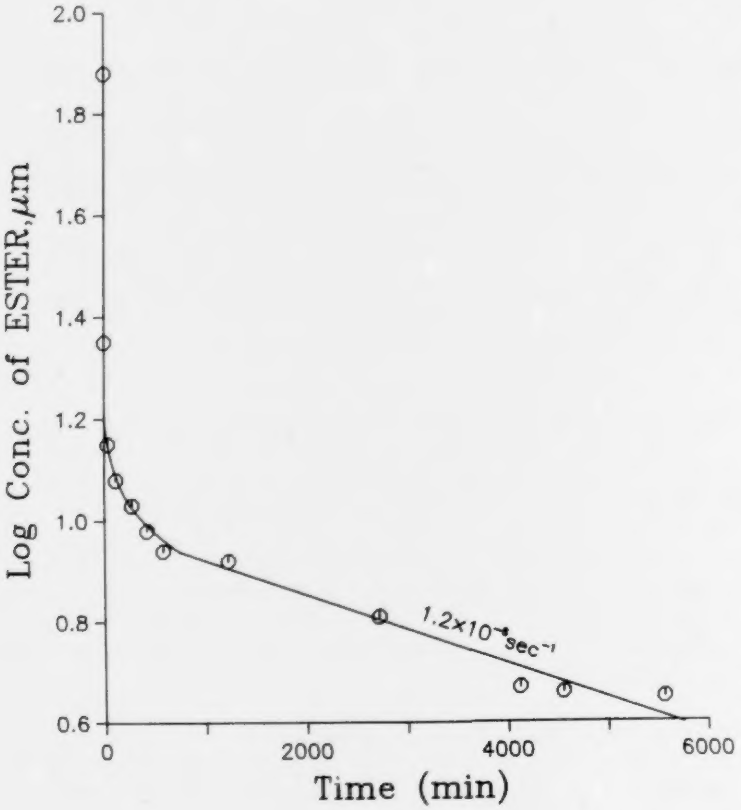

Figure 2. Hydrolysis of 2,4-D octyl ester in sediment/water at pH 10 from Wolfe (12).

Microbial Transformation

Transformations by microorganisms has received perhaps more extensive study than any other degradation process. It is only in the recent past, however, that microbial kinetic approaches have been pursued. Table 2 shows results obtained in our laboratory that have led us to suggest that the second-order

Table 2. Second Order Microbial Rate Constants (Average and Relative Standard Deviation for n Sites).

Compound	k_B (liter organism^{-1}hour^{-1})	n
2.4-D butoxyethyl ester	$5.4 \times 10^{-10} \pm 50\%$	31
malathion	$4.4 \times 10^{-11} \pm 60\%$	14
chlorpropham	$2.4 \times 10^{-14} \pm 42\%$	11
phenanthrene	$1.6 \times 10^{-10} \pm 75\%$	5
o - chlorotoluene	$2.7 \times 10^{-11} \pm 36\%$	5
phenol	$3.5 \times 10^{-10} \pm 60\%$	5
p-cresol	$2.7 \times 10^{-10} \pm 70\%$	5

microbial rate constants, k_B, are independent of site and population. The rate constants for the first three compounds (14) along with rate constants for several other (15) compounds that undergo hydrolytic transformation permitted establishment of the linear free energy relationship (LFER) shown in Figure 3 (16). These results have important implications for predictive efforts because alkaline hydrolysis constants are more readily available than microbial constants or can often be estimated from existing data. Thus, site dependence could be reduced to variation in population size.

To determine whether it was possible to develop similar relationships for other microbial transformation pathways, we have recently examined the kinetics and products of phenol oxidation by a pure culture of *Pseudomonas putida* (17). These conditions were chosen to optimize the possibility of developing a LFER rather than for environmental relevance. As can be seen from Table 3 and Figure 4, the rate constants do vary systematically with structure. Other data (17) not presented here also demonstrated that the rate is proportional to both population size and phenol concentration (i.e. second order) and that, for natural populations, the rate constants are reasonably independent of site.

In conclusion, scientific understanding of transport and transformation processes at the molecular level has advanced greatly over the past five years. Good tools are available for predicting those parameters that are essentially thermodynamic. Even the kinetics of simple transformation processes such as direct photolysis, hydrolysis, and microbial transformation are reasonably well understood.

There, however, remains the challenging problems of determining how these processes are influenced by association of the chemical with other environmental components as in sediment sorption, humic interactions and catalysis. Of these, the roles of catalysis and sorption are potentially important for a very wide range of chemicals. Interest in these phenomena is also stimulated by their role in transforming chemicals that pollute soil and ground water.

Much work also remains in understanding and applying the complexities of microbial kinetics to predictions of pollutant behavior. Many researchers still question even the application of kinetic equations to environmental problems. Certainly, the simple second order kinetic equations are not expected to describe the net rate where attached microbial populations

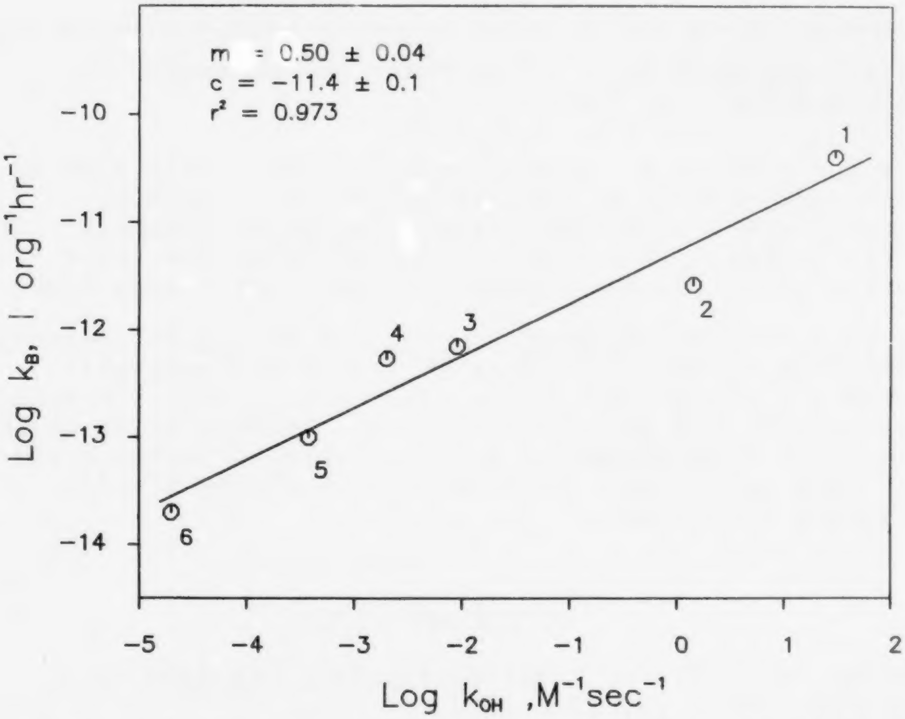

Figure 3. Correlation of second-order alkaline hydrolysis rate constants (27°) determined in distilled water with second-order biolysis rate constants (25°) determined in natural water samples (16). The compounds are: 1, n-butoxy-ethyl ester of 2,4-D; 2, malathion; 3, methyl benzoate; 4, methyl anisate; 5, methoxychlor; 6, chlorpropham.

Table 3. Rate Constants (K_b) for Microbial Degradation of Eight Phenols.

Compound	k_b (liter organism^{-1}hour^{-1})*
phenol (1)**	$(7.0 \pm 1.3) \times 10^{-12}$
p-cresol (2)	$(4.7 \pm 2.4) \times 10^{-12}$
p-chlorophenol (3)	$(1.7 \pm 0.9) \times 10^{-12}$
p-bromophenol (4)	$(1.6 \pm 0.8) \times 10^{-12}$
p-acetylphenol (5)	$(3.1 \pm 0.64) \times 10^{-13}$
p-methoxyphenol (6)	$(2.0 \pm 1.2) \times 10^{-13}$
p-nitrophenol (7)	$(1.0 \pm .54) \times 10^{-13}$
p-cyanophenol (8)	$(1.5 \pm .99) \times 10^{-14}$

*Mean and standard error of estimate for 10 runs.
**Compound number in Figure 4.

account for most of the transformation (18). This area of research continues to be plagued by lack of rigorous, unambiguous definition and careful testing of concepts. Thus, microbial process prediction will probably be the least convincing aspect of environmental models for a long time.

Finally, the development of LFER, or structure-activity relationships as they are often called in biology, will undoubtedly continue to receive considerable research attention for both biotic and abiotic processes. Demonstration of LFERs for microbial transformation will undoubtedly increase interest in this work and enhance the credibility of the kinetic relationship themselves.

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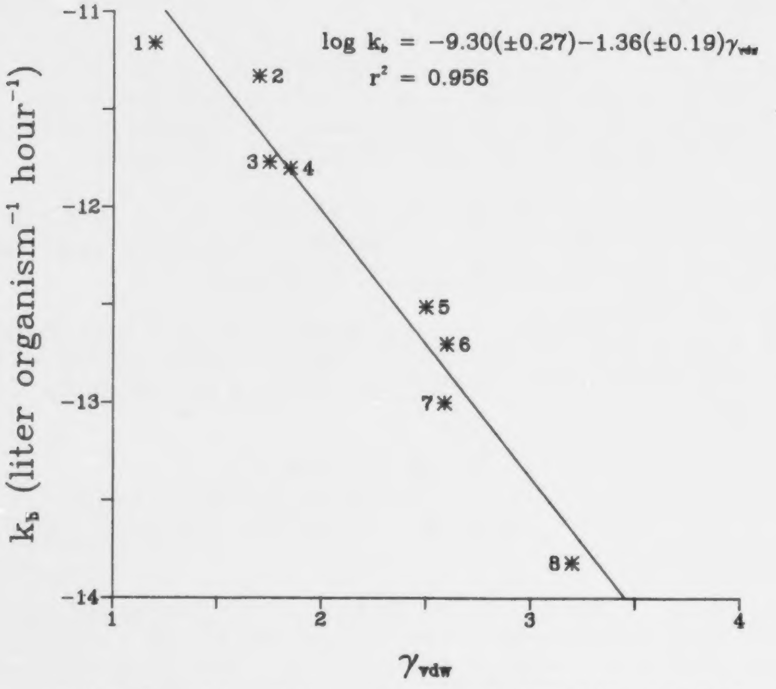

Figure 4. Relationship between the logarithm of the second-order microbial rate constant and van der Waals' radius of substituent group in Ångstrom. Compounds in Table 3.

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This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

PREDICTION OF PESTICIDE BEHAVIOR IN WATER

by

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A great body of data has been obtained on the behavior of various pesticides in natural waters. The purpose of this paper is to summarize the information available in the Soviet literature on the studies of the behavior in aquatic objects of those pesticides which are, or can be used under conditions of the Soviet Union. Special attention is concentrated on the processes of physical-chemical transformation of pesticides in water, particularly on the quantitative characteristic of their kinetics and mechanism, the influence of pesticides on the composition and properties of natural waters, prediction of pesticide content in water, and control and quality monitoring of natural waters polluted by pesticides.

Much attention has been given in the Soviet Union to chemicalization of its agriculture. For the period I970-I975, as a result of plant protection measures, an extra output has been obtained to a total value, on average, of 5.5-6.0 billion roubles per year (44). Undoubtedly, this demands appropriate nature protection measures (9).

Pesticides can reach water objects either as direct spray or dust applications using ground equipment or aircraft, or from the atmosphere, soil and plants. The behavior of pesticides in water bodies and streams depends on many factors, such as chemical structure of a substance, its water solubility, chemical interaction with water, stability to UV radiation, adsorption by suspended substances and bottom sediments, volatility from the water surface (55), amount and activity of microflora and hydrobionts, ability to accumulate in living aquatic organisms, water temperature, pH, the content of dissolved oxygen, biogenic elements, some specific pollutants, etc.

Surface runoff from a watershed is one of the main sources of pesticide entry into water bodies and streams (34). We considered the results of studying the entry of DDT and γ-BHC in surface runoff during spring flood and periods of rain. Surface runoff coefficients for a watershed with regulated flow were 0.02% for DDT and 0.06% for BHC, and for a watershed with natural flow 0.3% for DDT and 0.I% for BHC. The results obtained revealed that the runoff coefficients for organochlorine pesticides at natural watersheds and experimental runoff plots were less than one percent (53).

Using DDT as an example, the local, regional and global scales of atmospheric transport were considered, as well as pesticide fallout to the surface of soil. The regional transport was discussed from the measurement data on the vertical profiles of DDT concentrations in Fergana Valley and Khorezm Oasis (2).

The results of studies carried out for many years in the basin of the Middle Dnieper and in the area of the West Polesie (woodlands in the Ukraine) showed that the seasonal entry of organochlorine pesticides into water objects was nonuniform. In summer, pesticides were detected in 22% of the samples, in spring in 6I.2%, in summer in I7.6%, and in autumn in 8%, which coincided with periods of agricultural usage of pesticides and supported the fact of their predominant entry in surface runoff (IO).

Atmospheric transport is also one of the sources of surface water pollution by pesticides, particularly in the areas remote from sites of application (6).

Studying the removal of BHC, metafos/methyl parathion/ and chlorofos (together with DDVPh /0,0-dimethyl-0-(2,2-dichlorovinyl)-phosphate/) in surface runoff waters from experimental runoff plots IOO m^2 in size showed that the amount removed was directly proportional to the amount applied and the volume of water runoff. The removed amount of BHC did not exceed 0.03% of the amount applied, that of metafos 0.04%, and of chlorofos (together with DDVPh) 0.23%. According to the data of I973, half-life for BHC in the chestnut mid-loamy soil was 2 to 50 days, for metafos I.3 to I.8 days, for chlorofos 0.6 to 0.8 days, and for DDVPh I.4 to I.5 days (58).

Field studies in the Krasnodar Territory and South Ukraine show that the migration of anti-cereal herbicides(propanil, its metabolite 3,4-DCA, saturn /S-(4-chlorobenzil)-N,N-diethylthiocarbamate/ and ordram /molinate/) in the elements of irrigation systems is determined mainly by the physical-chemical properties of pesticides,edaphic-climatic conditions and peculiarities of the water regime of rice fields. As rice checks are flooded, part of herbicides from the surface of soil and plants enters the water. A certain amount of pesticides travels with filtration flow to the depth of soil. Herbicide residues from the fields reach the collector-drainage network in irrigation waste and ground waters.

As irrigation water is discharged, herbicides are removed from the field to the collector-drainage network with hydrobionts and microorganisms. The content of herbicides in the biomass of algae growing in the rice checks exceeds the concentration of toxicants in the water I000 to I0,000 times, and in the cells of bacteria approximately I00 times (8).

Under laboratory conditions, the rate of disappearance of rogor /0,0-dimethyl-S-(N-methyl-carbamoylmethyl)-dithiophosphate/ from natural waters was studied depending on various factors, such as temperature, pH, the presence of bottom sediments, and the type of water. It was found that a rise in the temperature of solution by I5°C accelerated the process of rogor transformation almost ten times(5I). The rate of rogor hydrolysis was shown to be directly proportional to pH of the solution: in an acid medium rogor was stable, whereas in an alkaline one it underwent a rapid hydrolysis. At pH 3.5 rogor hydrolysis was negligible and during a month its concentration remained almost constant. At pH 9.0 and temperature I6-I8°C there occurred saponification of 25% of the initial amount of rogor during the first thirty minutes and up to 64% on the third or fourth day. In the presence of bottom sediments, the process of rogor transformation in the water occurred in half the time. This process proceeded differently in various water objects. In the water of the Chirchik River, its intensity was twice that in the collector water, which was, according to the authors, due to the presence of a large number of vegetable and animal organisms in the river water.

A standard procedure of modeling the transformation of organic substances, including pesticides, in the artificially prepared "natural" water is described in (67). The method enables one to assess rapidly the persistence of pesticides in the "natural" water under reproducible conditions.

When studying on models the kinetics of disappearance of thiocarbamate herbicides from natural water, it was found that under dynamic conditions the degradation of yalan /molinate/ and saturn was half as rapid again as, or twice that under static conditions. This resulted from an increase in the enzymatic activity of water mass due to the entry of enzymes from the cells destroyed in a turbulent flow (20).

Over a temperature range 5-30°C, the rate of disappearance of thiocarbamate herbicides (K) from natural water sharply increased: at 5°C it was 0.04 day^{-I} for yalan and 0.03 day^{-I} for saturn, whereas at 30°C 5.63 days^{-I} and 3.18 days^{-I}, respectively.

Sorption by bottom sediments varied from 5I% to 90%(on average, 65%) of the initial content for yalan and from I4% to 79% (on average, 47%) for saturn (62).

Laboratory studies showed that the persistence of the derivatives of phenoxyalkylcarboxylic acids and thiocarbamates increased in the order of 2,4-D chlorocrotyl ester, 2,4-D octyl ester → 2-methyl-4-chlorophenoxypropionic acid (2M-4ChP), 2-methyl-4-chlorophenoxybutyric acid (2M-4ChB) → eptam/S-ethyl-N,N-dipropyl thiocarbamate/ → tillam/S-propyl-N-ethyl-N-butyl thiocarbamate/. Relatively increased stability of thiocarbamates can be accounted for by the presence of a methyl group at ortho-position in the phenolic ring(55).

Unlike the derivatives of phenoxyalkylcarboxylic acids, thiocarbamates are volatile compounds, volatility of eptam being I.57 g/m^3 and that of tillam 0.II g/m^3. Therefore their disappearance from water was due to biochemical oxidation and also their ability to volatilize to the atmosphere (55).

In model experiments, the degradation rate was studied in the water of irrigation waste water collectors in the Krasnodar Territory for the following herbicides: propanil, its metabolite 3,4-dichloroaniline (3,4-DCA), ordram and benthiocarb /saturn/. Their rate of transformation was in the order of propanil $>$ 3,4-DCA $>$ benthiocarb $>$ ordram. The rate constants of transformation at a temperature I8-27°C were 0.45, 0.058, 0.042 and 0.0I3 day^{-I} ,respectively.

It was shown that as mineralization of the water increased from 5I4 mg/l to 43 g/l, the rate of disappearance of propanil decreased by over three times ($K = 0.I3\ day^{-I}$). In the presence of bottom sediments (2 g/l), the rate of disappearance of ordram was half as much again as in absence of bottom sediments (60).

Under laboratory conditions, the kinetics of metafos disappearance from the water of the Severny Donets River and Dnieprodzerzhinsky Reservoir was studied. Microorganisms of water and bottom sediments were shown to have a dominant role in metafos transformation, while its chemical destruction was insignificant. Depending on specific conditions of natural waters,the rate constant of metafos hydrolysis varied from $5.93 \times IO^{-3}$ $days^{-I}$ to I.92 $days^{-I}$ (I5,30,39,72,75).

Complex physical-chemical and biochemical processes of transformation of organic and inorganic substances occur in water objects. The mechanism of pesticide transformation in natural waters is determined mainly by the structure of a substance and the prevailing processes. There are two main routes of this transformation: I) via a number of successively oxidized compounds which are simpler in structure; and 2) via the formation of humic acids or other more complex and stable substances.

The basic types of biochemical pesticide transformations in natural waters are oxidation,reduction, hydrolysis, dehalogenation, isomerization, and formation of polymers and conjugates with the substances of hydrobionts.

The most widespread are reactions of oxidation in water of individual functional groups entering into the composition of pesticides. Compounds of aliphatic series, such as organophosphorus substances, 2,2-dichloropropionic acid (dalapon), trichloroacetic acid, etc., as well as hydroxyl-containing compounds, such as carbolic acid,cresols, etc. are, as a rule, easily oxidized ,unlike the derivatives of benzene and naphthalene which do not contain in the ring sulfur or nitrogen as a substituent of oxygen.

Reductive reactions were observed under anaerobic conditions for 2,4-D (acid), DDT, lindane, thiofos /parathion/ and other pesticides (5,36).

The major transformation route for BHC in natural waters is dehalogenation. The first product of BHC transformation is pentachlorocyclohexane released as several isomers. In the subsequent metabolism,observed the formation of all possible isomeric di-, tri-, and tetrachlorophenols is observed (36,59). Metabolism of the herbicide propanil in water begins with the process of dehalogenation (36,52).

Organophosphorus pesticides and their metabolites (36,46, 37), as well as the derivatives of phosphoric, thio-, dithiophosphoric and phosphonic acids (for example, chlorofos) (36, I8,42,3,70) form conjugates with the products of the vital activity of plants.

Under the action of UV radiation, oxidation of thionic sulfur of the derivatives of thiophosphoric acid, such as parathion (thiofos), metafos (26,34,45), methyl nitrofos /fenitrothion/ (II,28,47) and trichlorometafos-3 /O-methyl-O-ethyl-O(2,4, 5-trichlorophenyl)-phosphorothioate/ (26,43) can occur, as well as isomerization to S-ethyl- and S-(4-nitrophenyl)-derivatives.

In the Soviet Union, a ban has been imposed on the use of DDT. However, its extensive use in the I950s and I960s, as well as high stability in the environment are responsible for the fact that DDT is still being detected in certain regions of the country.

The results of some studies (34,7I) indicate that in the south area, there occurs a relatively rapid destruction of DDT under anaerobic conditions, as the soil is flooded with water. Under aerobic conditions, DDT destruction proceeds slower due to a different mechanism of transformation. In the first stage under anaerobic conditions, there occurs DDT reduction to DDD and a rapid destruction of the latter,whereas under aerobic conditions, the first stage of DDT destruction is the formation of a highly stable I,I-dichloro-2,2-bis(4-chlorophenyl)ethylene.

DDT mobility in soil is extremely small (less than I0 cm per year at a temperature 25°C and annual rainfall I500 mm), since it is readily sorbed (up to 98%) by clays from aqueous solutions, that inhibits its leaching to lower layers and prevents evaporation to the atmosphere (no more than 0.I kg of DDT evaporates annually from an area of I hectare) (36,55).

DDT is capable of accumulating in aquatic living organisms, such as plankton, invertebrates, various species of freshwater and marine fish (40). The presence of polychlorinated biphenyls (PCB's) in water enhances toxic effects of DDT on phytoplankton (36). DDT from water can penetrate into plants and accumulate in small amounts in fruits (49) and in relatively high concentrations in leaves.

Under laboratory conditions, DDT uptake and accumulation by Ceratophyllum (hornwort) and Potamogeton perfoliatus were studied (74). As DDT content in water increased to 2 mg/l, concentrations in the plants per I g of raw substance gradually reached I04 μg for DDT, 4I.4 μg for DDD and 3.3 μg for DDE. A high content of DDT in tissues of the plants had a strong toxic effect on the vital activity of Potamogeton: the plants had chlorosis and a gradual necrosis of leaf tissues. The occurrence of DDT metabolites in the plants and water was likely due to a partial dechlorination of DDT yielding less toxic DDD and DDE. With increasing concentration of DDT in the water of experimental aquariums, on the eighth day after its application there occurred a three-times decrease in the content of water-dissolved oxygen (to 2.9 mg O_2/l) and a gradual decrease of pH of the water(from 7.4 to 5.7 in the aquariums with Potamogeton and from 8.0 to 6.3 in those with hornwort).

Pesticide stability depends on their ability for hydrolysis,i.e. chemical interaction with water. In most cases, hydrolysis leads to pesticide decomposition to yield less toxic compounds. Hydrolysis of organophosphorus and other pesticides, particularly herbicides, such as propanil, carbofos/malathion/ (27,75), phthalofos /O,O-dimethyl-S-phthalimidomethylphosphorodithioate/ and dieldrin proceeds most easily in moist soils (36,68). The rate of pesticide hydrolysis increases with increasing water temperature and pH (35,36).

Oxidative hydrolysis of the derivatives of dithiophosphoric acid proceeds in water very actively. The rate of transformation of dithiophosphates, such as menazon /O,O-dimethyl-S-(4.6-diamino-I,3,5-triazin-2-ylmethyl) phosphorodithioate/, fozalon /benzophosphate/, phthalofos, fencapton /O,O-diethyl-S-(2,5-dichlorophenylthiomethyl) phosphorodithioate/ and cidial /phenthoate/, increases most appreciably under ultraviolet light (23). Metabolism in water of phosphamide /dimethoate/ and formothion /O,O-dimethyl-S-(N-methyl-N-formylcarbamoylmethyl) phosphorodithioate/ (36,29) extensively used in the Soviet Union to control pests of cotton and some other plants begins with oxidative hydrolysis. For phthalofos and benzophosphate this process is slower than for carbofos, phosphamide and formothion (36,50,28,44). Menazon (36,46) and bipyridylium herbicides, such as diquat and bipyridylphosphate /I,I'-dimethyl-4,4'-bipyridylium-dimethylphosphate/(36,69), are characterized by even larger stability.

Dealkylation and hydrolysis are the most important degradation pathways of such thiocarbamates as diallate, triallate, molinate, eptam, vernolate, tillam, cycloate, benthiocarb(saturn), etc. Benthiocarb concentration in the water of a river flowing near the treated rice checks did not exceed 3 mg/l and rapidly decreased during the first two weeks after treatment (36,33).

The main products of thiocarbamate oxidation by microorganisms are sulfoxides (36,33), which are hydrolytically unstable in aquatic systems. At pH over 7.0 they are unstable even at room temperature.

Diallate, triallate and eptam were found to be capable of stimulating the reproduction of aerobic saprophytic bacteria and inhibiting the processes of nitrification for some time (32,I6). Migration of eptam and tillam through the soil profile was significant (36,56).

When molinate was applied as emulsion, it was detected in the water of rice checks during a week after application at a concentration of 0.2 mg/l, while as a granular formulation, during I5 days at a concentration of 0.03-0.08 mg/l (36,64).

At pH close to 7.0 the derivatives of arylhydroxyalkanecarboxylic acids are rather stable in aqueous solutions. As temperature in an acidic or alkaline medium increases, hydrolysis proceeds through the ether linkage to form phenol and a corresponding acid (36).

A certain role in water body self-purification of pesticides is assigned to the processes of their volatilization from the water surface (I7). However, the losses of pesticides from water due to their transformation under UV light are considerably more intensive. Research into the kinetics of pesticide photolysis and identification of their possible metabolites has received attention of many investigators (for,example, (22)). When exposed to ultraviolet, polychloropinene and polychlorocamphene which are stable in water are degraded to form several nonidentified products. Under the influence of UV light, polychlorocamphene may decompose releasing hydrogen chloride. In natural conditions,the amount of polychlorocamphene in the arable soil layer decreased by 50% in twelve months, whereas upon UV irradiation in 45 min. Polychloropinene is a persistent pesticide: one year after the soil treatment its amount decreased only by I7% of the initial content. Half-life of polychloropinene under UV light is I.9 hrs. (2I).

The rate and mechanism of photochemical transformation of ten organophosphorus pesticides were studied under laboratory conditions upon irradiation,using a lamp ПРК-4 (23). Half-lifes of the pesticides varied from 4 min. (bytex/fenthion/) to 630 min. (saifos/menazon/).

Some herbicides, such as propanil, are degraded under the action of UV light (I). As solution is stirred and saturated with oxygen, no significant increase occurs in the degradation rate of propanil, probably, due to the specific character of the mechanism of photochemical degradation of the herbicide with chlorine atoms in the benzene ring: the reaction of hydrolytic dechlorination yielding oxycompounds takes place.

As propanil undergoes photochemical decomposition,this does not give rise to appreciable amounts of its metabolite 3,4-dichloroaniline which is the main intermediate product under natural conditions. It is likely that in this case 3-chloro-4-hydroxyaniline, 3-hydroxy-4-chloroaniline and 3,4-dihydroxyaniline are formed,which are easily oxidized by oxygen of the air (I).

Given the photolytic stability of a herbicide and illumination conditions of the climatic zone under consideration,it is possible to estimate the amount of the substance which can remain in the water phase, taking into account the irrigation regime of rice checks (I3,I4).

Clay minerals and organic substances of bottom sediments participate in pesticide sorption which is also affected by water temperature and pH. The sorption may proceed by the following major mechanisms:

I. Physical sorption and formation of hydrogen bonds between neutral molecules of pesticides and active centers on the surface of colloid particles of bottom sediments, occurring, as a rule, at pH close to 7.0.

2. Ionic sorption of cationic forms of pesticides that proceeds due to ion exchange with cations located on the surface of clay minerals and colloids of organic polyelectrolytes, and increases with decreasing pH.

3. Formation of pesticide complexes with hydrogen ions on the surface of micelles of bottom sediment colloids.

The value of pesticide sorption is directly proportional to organic matter content in bottom sediments, cation-exchange capacity and specific surface of natural sorbents (63).

The sorption processes are affected by the chemical structure of organic matter. Thus for the derivatives of sym-triazine replaced at position 2, sorption decreases in the order of $SC_2O_5 > SCH_3 > OCH_3 > OH > Cl$. Sorption of dialkylamino-compounds proceeds more actively than that of monoalkylated derivatives and decreases in the order of tertiary $C_4H_9 >$ secondary $C_4H_9 > C_2H_5 >$ iso-$C_3H_7 > CH_3 > C(CH_3)_2CN$.

A method has been proposed for determining the sorption characteristics of organic matter including pesticides such as propanil; 2.4-D; 3.4-DCA and 2.4-dimethyltetrachloroterephthalate (2,4-DChPh), on samples of soils and clay minerals. It is necessary that extreme conditions be revealed, in which the sorption processes occur depending on the following main factors: liquid-to-solid phase ratio, time during which the liquid and solid phases are in contact, pH and temperature of aqueous solution, sorbent moisture and sorbate concentration. It has been noted that the results of laboratory modeling enable one to establish a number of regular patterns in the behavior of pesticides in soil and aquatic environments(24,25).

As equilibrium between solution and sorbent is reached instantaneously, Freundlich sorption isotherm can be used as a model of equilibrium. If equilibrium is not reached instantaneously, two kinetic models of the corresponding reaction can be proposed. In the first of them, it is assumed that the pore space through which solution flows is homogeneous, whereas sorbent is inhomogeneous. In the second model, the presence of open (through) and closed (blind) pores is taken into account, and sorption is assumed to proceed equally throughout the pore space. Application of the proposed mathematical models describing the dynamic sorption of pesticides in soil enables one to determine most accurately the constants of isotherm and the rates of exchange(41).

Under laboratory conditions, the sorption of propanil, 3,4-DCA and yalan was studied on four samples of soils of the Krasnodar Territory: sand, loamy sand, light clay and clay loam. Sorption equilibrium in the "soil- pesticide solution" system was reached in a few minutes after the beginning of phase interaction, which appeared to be caused by pesticide sorption mainly on the surface of sorbents due to Van der Waals forces. Pesticide sorption by soils was adequately described by the Freundlich equation. A relative sorptive capacity of soils decreased in the order clay loam > light clay > loamy sand > sand. The change in sorptive capacity of soils was directly proportional to humus content in the sorbents (from 0.05% in sand to 2.7% in clay loam). The extent to which pesticides were sorbed by the sorbents studied was in the order of propanil > 3,4-DCA > yalan (76).

In aquatic objects, pesticides affect a wide variety of biological processes thus disturbing ecological equilibrium in the aquatic environment. This is evidenced indirectly by variations in oxygen balance, the content of water-dissolved oxygen, pH and other indices of water composition and properties.

Exposure to pesticides can produce changes in plankton dominants, as well as in the order of ecological successions and the structure of plankton communities.

Low concentrations of pesticides may intensify decomposition of individual alga species or complexes, acting as eutrophication agents. As a result of destruction of dead "organic matter", there occurs an increase in the concentration of carbon and nitrogen-containing compounds in water, which ultimately accumulate as nitrates readily assimilated by algae (7). The process of nitrification is strongly inhibited by tillam (I0.0 mg/l) and 2,4-D chlorocrotyl ester (20 mg/l): the concentration of nitrites and nitrates does not increase during I5 days (55).

After a rice check was treated with saturn at a concentration in water of 2.I5 mg/l, a sharp decrease was observed in numbers of microorganisms (3.6-times), biomass (7.I-times) and species composition of zooplankton (3I).

Studies on the models of microchecks revealed that at concentrations up to 0.2 mg/l, yalan did not exert toxic effects - quite the reverse, it stimulated the development of bacterioplankton. Contact with yalan changed the species ratio of bacteria, fungi and actinomycetes. Heterotrophic ammonifiers intensively assimilated yalan and increased their numbers 3 to I5 times compared to natural populations. A high degree of correlation was found between yalan concentration in water, potential catalase activity of the aquatic environment and saprophyte numbers (6I).

Little data have been published that characterize quantitatively the influence of pesticides on the composition and properties of natural waters. Predicting the content of pesticides in water is possible if regularities of the processes affecting pesticide concentration are studied quantitatively. A number of prediction models describing pesticide migration in water bodies and streams have been proposed. Since information is lacking on the quantitative characteristics of complex physical-chemical and biochemical processes of transformation which depend on numerous parameters, investigators, as a rule, have to adopt a number of assumptions in their models. This inevitably affects reliability of the obtained prediction data.

The principles of mathematical modeling of pesticide migration in some components of the environment based on statistical analysis are discussed in (66), where the authors concentrate their attention on the models for calculating the amount of pesticide remaining in a plant under given conditions and in various periods of time after treatment. In all, they considered schematically 45 factors which determine the content of pesticides in various media and the dynamics of migration between them. The methods for calculating single and mean daily maximum concentrations of pesticides in sanitary-domestic waters and streams appear to be promising.

A mass-transfer equation has been proposed to predict the chemical composition of underground (drainage) waters and migration of the carbamate insecticide sevin /carbaryl/ in them (4) . The investigators took into account the processes of sevin entry from the surface and its movement with filtration flow, as well as the physical-chemical processes of its adsorption by, and leaching from soil. Under laboratory conditions, they determined by a statistical scheme the type of sorption, the rate of sorptive exchange,maximum sorptive capacity of the solid phase, and partition coefficients for the studied sandy-clayey sediments. Unfortunately, the authors have not compared the results of prediction calculations of sevin content in control sections with the data of field observations carried out in irrigated agricultural plots in Chardzhouskii Oasis, Turkmenistan. Therefore it seems impossible to assess reliability of the calculated prediction data obtained by the model proposed.

Chromatographic methods have been suggested to be used not only for a separate determination of pesticide residues(the derivatives of phenoxyalkane-carboxylic acids), but also as a source of useful information that can be applied to predict the behavior of pesticides in aquatic objects. Water body pollution will be insignificant in the case of pesticides with small R_f and large volumes of retention due to their rapid sorption by suspended substances and bottom sediments. At the same time, pesticide inactivation proceeds more rapidly at small R_f, which results in decreasing probability of secondary water pollution (73).

According to the authors of (65) concerned with determination of the role of experimental hygienic studies in prediction of pesticide behavior in the environment, the key factors characterizing the level of accumulation of substances in environmental objects and their possible migration in various ecocenoses are persistence and mobility. The authors suggested determination in model installations of the quantitative characteristics of pesticide persistence and migration mobility in water, soil and plants due to hydrolysis, oxidation, photodecomposition, microbial breakdown, etc. The assumption was supported of running water in rice checks and discharged irrigation water, rather than filtration,being the major routes of propanil and yalan entry into irrigation waste water canals. In model experiments, yalan persisted in water during 60 days, whereas in water with meadow-bog soil up to 30 days.

A first-order equation was used for prediction calculations of pesticide content in water. The discrepancy between the actual and calculated data did not exceed 19% (57).

Prevention of pollution of aquatic objects by pesticides can be effective if the complex of measures is taken at all stages of pesticide production, transportation, storage, application, etc.

The use of granular pesticides with inert fillers is of great water-protective significance. In this case, granules gradually release the pesticide into the soil, that prevents its removal by water flow over the surface during periods of rain and promotes the process of its transformation or sorption by the soil.

Improvements in spraying techniques and equipment appear to be promising. The use of ultrasmall-volume spraying(USVS) by reducing the diameter of droplets which are formed from spraying solution, permits the amount of pesticides applied to be reduced substantially (hundreds of times) and at the same time, increases their effectiveness.

First experiments on the use of foam-spraying also give promising results from the view point of decreasing amount of pesticides applied (70).

In the last few years, research and experimental field works have been successfully carried on with the aim of developing recommendations to prevent, or at least decrease substantially the removal of pesticides and other pollutants in surface runoff from agricultural land to aquatic objects.

The general principles of constructing riverside water-protective zones through the use of the system of defensive strips, that are being developed, and the complex of measures of water-protective reclamation, as well as erosion-preventive agricultural and hydraulic engineering will allow in future,according to some investigators, a purposeful control of natural water quality by a simultaneous protection of aquatic objects from pollution by pesticides and biogenic substances, silting as a result of washing away of arable layer subject to water and wind erosion, etc.

Employment of the ability of some pesticides to be actively sorbed by bottom sediments, suspended particulate matter, sand and soil appears to be promising. Pesticides sorbed by soil and sand undergo natural transformation processes during the inter-vegetation period. As a result, the adsorptive capacity of natural sorbents is restored. Technical realization of this principle of protecting aquatic objects from adverse effects of collected discharges of irrigation return waters under conditions of Central Asia has already given positive results (19, 48, 12, 37, 77).

Almost complete destruction of herbicides of the 3,4-D group and their metabolites can be attained by holding irrigation return waters, prior to their discharge to aquatic objects, for 2-3 weeks in reservoirs adapted specially for this purpose and formed by cutting off portions of firths using dams, or by broadening the terminal portions of discharge collectors (38).

Substantial decrease in the content of herbicides in water occurs due to their natural destruction in the flooding layer of fallow field, to which it is recommended to pump the water from the collector-drainage network (38).

Thus, to predict the behavior of pesticides in water it is essential that information be available on the quantitative characteristics of the main processes of their transformation and migration in natural waters. Experience in the work on aquatic objects supports the conclusion that it is advisable to study the processes of pesticide transformation by the scheme: "aquatic object - modeling - aquatic object".

The kinetics of pesticide transformation in water depends on numerous factors and interaction of various processes. Therefore it is essential that the methods of cybernetic modeling be used to develop prediction techniques and ultimately, to perform an effective control of the "pesticide - environment" system with the aim of preserving the purity of human habitat.

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Influence of Natural Substances on the Photoreactivity of Pesticides in the Aquatic Environment

by

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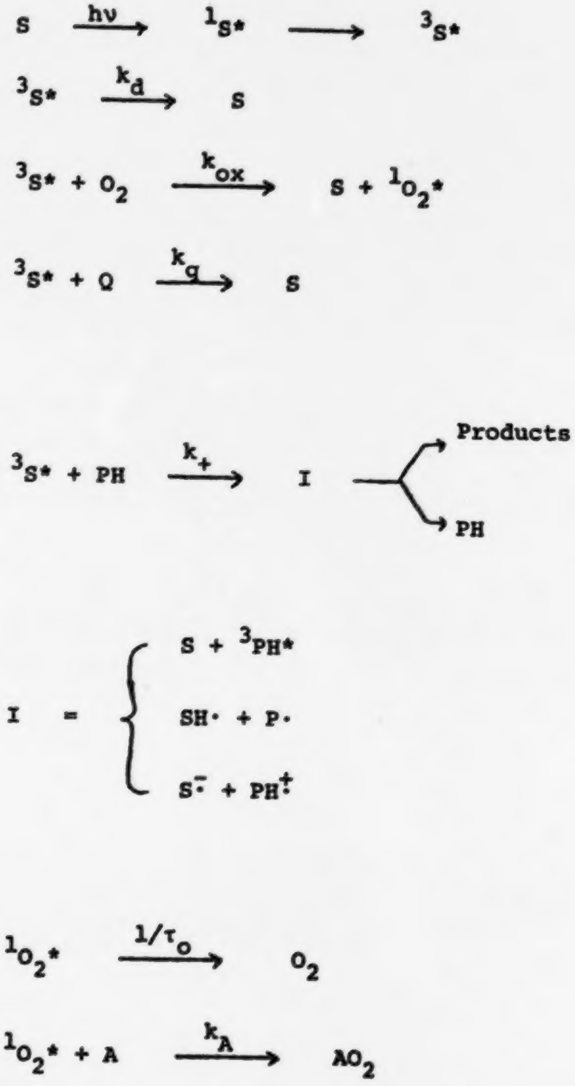
Environmental problems associated with the use of certain pesticides in the United States have prompted research efforts oriented towards forecasting the behavior of such chemicals in aquatic environments. This paper emphasizes investigations of sunlight-induced photoreactions of pesticides and other synthetic chemicals in natural waters. The overall objective of this research has been to define kinetic expressions and parameters that can be employed to predict photolysis "rates," or conversions per unit time, under the wide variety of conditions that exist in aquatic ecosystems. Results of these studies are being used in computer models that integrate rate and equilibrium data to provide estimates of exposure concentrations of pesticides in various environmental compartments (1).

Past studies have indicated that photochemical transformations occur upon direct absorption of light by a reactive chemical or, alternatively, through indirect processes that involve light absorption by another substance that is in the system with the reactive chemical. The photolysis rate of a pesticide in a water body equals the sum of the rates of its various competing direct and indirect photoreactions. Procedures have been developed for predicting direct photolysis rates of chemicals at low concentrations in air-saturated distilled water (2,3). Recently our attention has turned to the more complex problem of quantitating the effects of substances indigenous to aquatic environments on photolysis rates and products. Such natural substances influence photolysis rates of pesticides in aquatic environments through attenuation of sunlight in water bodies, through initiation of indirect photoprocesses, and through physical or chemical interactions that alter the speciation or microenvironment of pesticides. Recent research on these various effects is discussed here, with emphasis on studies of the influence of humic substances and suspended sediments on photoreactions of trace organic chemicals.

Influence of Humic Substances on Photoreaction

Indirect Photolysis

Several studies have demonstrated that photolysis rates of certain organic chemicals are enhanced in the presence of humic substances (4-10). In some cases, chemicals that are unreactive in distilled water were found to photoreact rapidly in solutions of humic substances or in natural water samples (7). Usually, when photolysis rates were enhanced by humic substances, different photoproducts also were formed (4,5,7). The studies have indicated that humic substances are capable of photosensitizing several types of organic photoreactions. A scheme that summarizes the various reaction pathways is shown in Figure 1, where S represents the part(s) of humic substances that acts as a sensitizer and S* represents the sensitizer in its electronically excited state. The excited sensitizer can transfer energy to molecular oxygen, O_2, to form singlet oxygen, $^1O_2*$, a species capable of oxidizing certain types of pesticides represented by A (6). Reactions involving singlet oxygen are



$$S \xrightarrow{h\nu} {}^1S* \longrightarrow {}^3S*$$

$${}^3S* \xrightarrow{k_d} S$$

$${}^3S* + O_2 \xrightarrow{k_{ox}} S + {}^1O_2*$$

$${}^3S* + Q \xrightarrow{k_q} S$$

$${}^3S* + PH \xrightarrow{k_+} I \to \text{Products} \quad ; \quad I \to PH$$

$$I = \begin{cases} S + {}^3PH* \\ SH\cdot + P\cdot \\ S^{\bar{\cdot}} + PH^{\dot{+}} \end{cases}$$

$${}^1O_2* \xrightarrow{1/\tau_o} O_2$$

$${}^1O_2* + A \xrightarrow{k_A} AO_2$$

Figure 1. Skeletonized mechanism for pesticide reactions photosensitized by humic substances.

called "oxygenations." Direct interactions between S* and pesticide include energy transfer, hydrogen transfer, or electron transfer to form various reactive intermediates I (7). At pesticide concentrations that are very low, the photosensitized reactions can be described by rate expressions that are first order with respect to pesticide concentration [P]; that is, the rate equals k_S [P] where k_S is the rate constant, which is expressed in units of reciprocal time.

Oxygenations photosensitized by humic substances have been studies in detail (6-9). Zepp and coworkers (6,7) have reported oxygenations of furans and sulfides in sunlight (Figure 2). The oxygenation of 2,5-dimethylfuran (DMF) was studied to obtain detailed information about photosensitization by humic substances. The DMF studies were conducted at sufficiently low concentrations to insure that the reaction was not complicated by the competing free radical reactions that can be initiated by the peroxide products (9). Several mechanistic tests established that the oxidation of DMF in natural water samples was mediated by singlet oxygen (6). For example, the oxygenation of DMF in a swamp containing dissolved humic substances was affected by DABCO (1,4-diazabiclo[2,2,2]octane) and deuterium oxide in the same way as the photo-oxygenation of DMF sensitized rose bengal, a known singlet oxygen sensitizer (Figure 3). Other studies involving DMF as a substrate indicated that rates of sunlight-induced oxygenations sensitized by the humic substances in river water were independent of hydrogen-ion activity from pH 5 to pH 10 (18) (Figure 4).

Because humic substances are known to be mixtures of refractory chemicals derived mainly from plant decay, it seemed likely to us, as we started studies of sensitized reactions, that humic substances from different locations would exhibit very different photochemical behavior. Results of several studies,

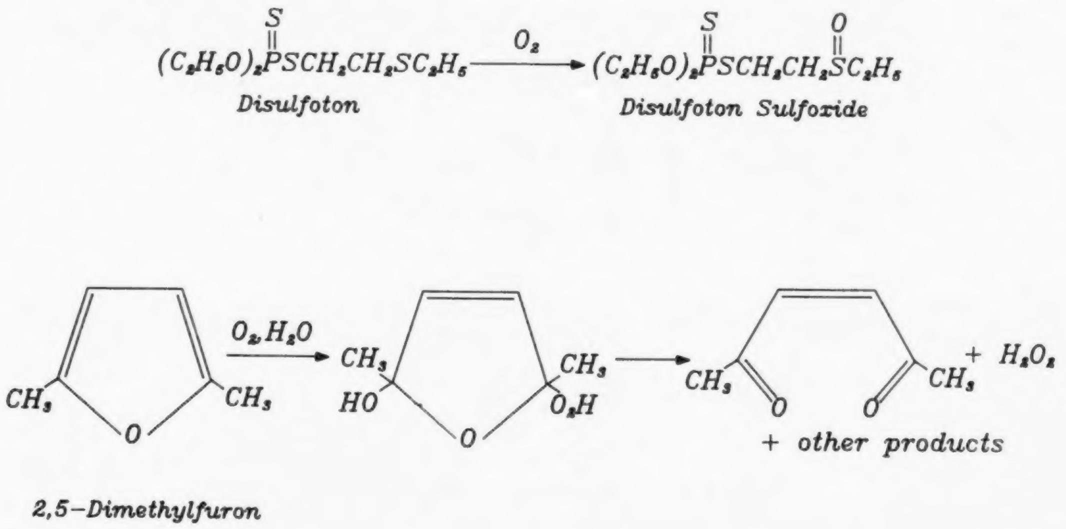

$(C_2H_5O)_2\overset{S}{\overset{\|}{P}}SCH_2CH_2SC_2H_5 \xrightarrow{O_2} (C_2H_5O)_2\overset{S}{\overset{\|}{P}}SCH_2CH_2\overset{O}{\overset{\|}{S}}C_2H_5$
Disulfoton
Disulfoton Sulfoxide
O_2, H_2O
CH_3
CH_3
O
CH_3
HO
CH_3
O_2H
O
CH_3
O
O
CH_3
+ H_2O_2
+ other products
2,5-Dimethylfuron

Figure 2. Photooxygenations sensitized by humic substances in water (7).

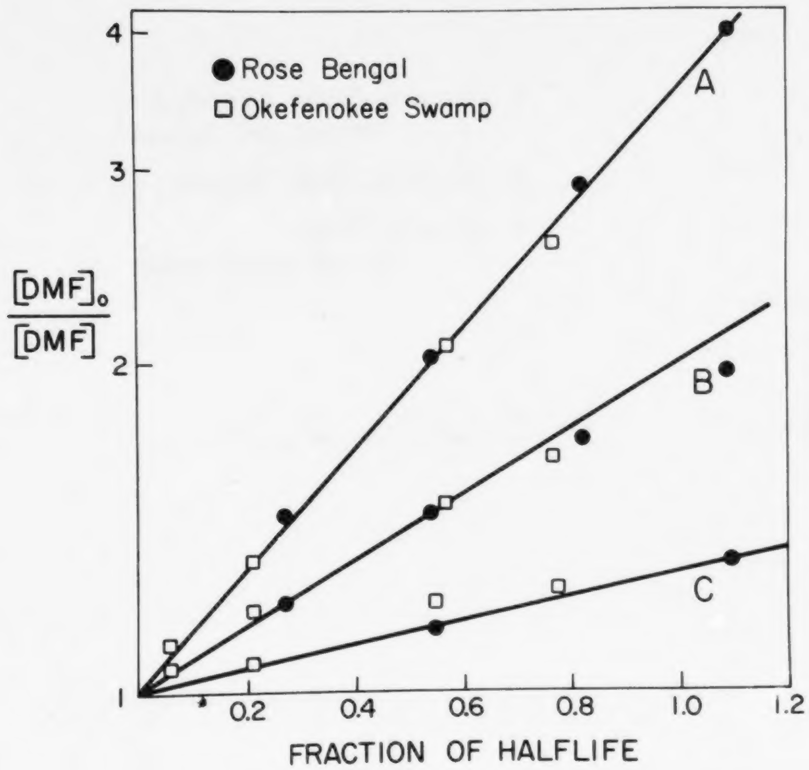


Figure 3. Effect of DABCO and deutrium oxide on photooxygenation of 2,5-dimethylfuran (DMF) in Okefenokee Swamp water and in distilled water containing rose bengal; initial DMF concentration $[DMF]_0$, 1.0×10^{-4}M. Duration of light exposure expressed as fraction of half-life compared with systems with no added DABCO or deuterium oxide, B, 1:1 mixture of swamp water or 10^{-4}M aqueous rose bengal with 0.019 M aqueous DABCO. Light source was a 450-watt medium pressure mercury lamp; light was filtered through Corning 7-83 glass filters to isolate 366-nm line (Ref. 6).

however, have indicated that just the opposite is the case. Detailed studies with sunlight or monochromatic light indicate that humic substances in a wide variety of water bodies or humic and fulvic acids extracted from soils have very similar photosensitizing capacities (7,8). These similarities are illustrated by comparisons of kinetic data obtained for photosensitized oxygenations of DMF and the insecticide disulfoton in sunlight (Table 1) (7). Similar findings have been reported for other types of photoreactions that are sensitized by humic substances (4,7) including a cis-trans isomerization that involves electronic energy transfer from sensitizer to 1,3-pentadiene and reactions involving hydrogen transfer from aniline to sensitizer (Figure 5). The reaction shown for aniline also occurs with the herbicide metabolite 3,4-dichloroaniline in competition with its direct photoreaction (4).

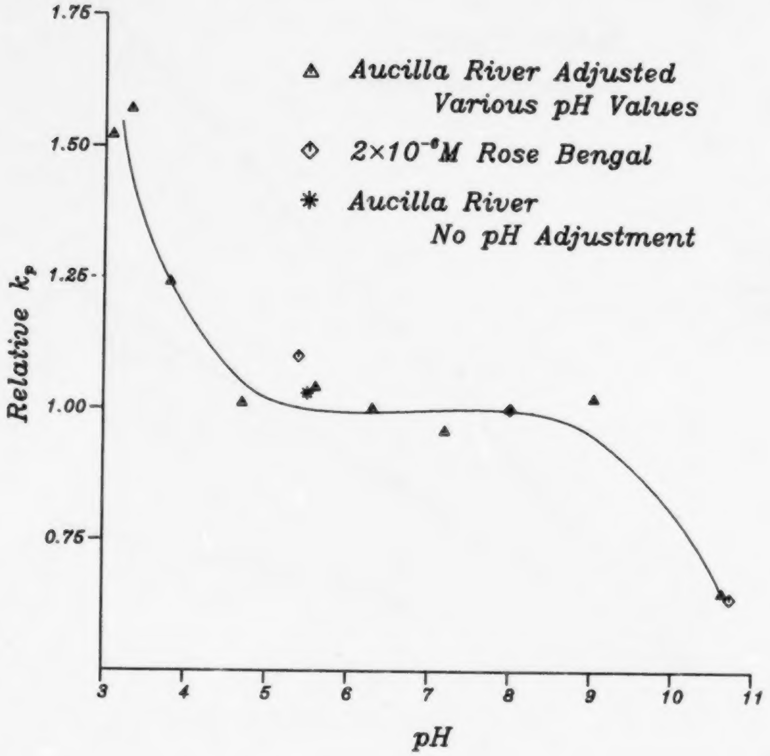


Figure 4. pH dependence of photosensitized oxygenation of 2,5-dimethylfuran (8).

To more quantitatively determine the effects of varying reaction conditions on the photosensitizing capacities of various humic substances, response functions, $X_{s,\lambda}$, have been determined for the photosensitized oxygenation of DMF employing monochromatic light. Response functions were computed using Eq.1:

$$X_{s,\lambda} = \frac{k_{s,\lambda}}{E_0^{av}(\lambda)} \qquad (1)$$

where $k_{s,\lambda}$ is the observed first order rate constant for the oxygenation and $E_0^{av}(\lambda)$ is the average irradiance in the reaction cell at wavelength λ. As predicted by theory (8), experimental results indicated that X_s for the DMF reaction is directly proportional to the concentration of humic substance. Kinetic studies at various wavelengths indicated that response functions for photooxygenation of DMF sensitized by humic substances in the Aucilla River and by soil-derived humic acids were the same within a factor of 2 in the near

Table 1. KINETIC DATA FOR OXYGENATION REACTIONS PHOTOSENSITIZED BY HUMIC SUBSTANCES IN WATER EXPOSED TO SUNLIGHT (Ref. 7)

	Relative Rate Constant[a,b,c]	
Humic Source	2,5-Dimethylfuran[d]	Disulfoton[e]
Distilled Water	<0.01	<0.1
Aucilla River, FL	1.0	1.0
Okefenokee Swamp, GA	1.13 ± 0.32 (4)	--
Quincy Bog, NH	1.52 ± 0.08 (4)	--
Williamson River, OR	1.22 ± 0.40 (4)	--
Fulvic Acid, CA[f]	1.52 ± 0.40 (3)	1.2 ± 0.2 (3)
Contech Fulvic Acid[f,g]	0.98 (1)	1.1 ± 0.1 (2)
Aldrich Humic Acid[f,g]	1.21 ± 0.17 (6)	1.1 ± 0.4 (3)
Karl Roth Humic Acid[f,g]	0.50 ± 0.25 (4)	
Fluka Humic Acid[f,g]		
Lot A	0.81 (1)	1.2 ± 0.4 (2)
Lot B	0.68 (1)	1.15 ± 0.4 (2)
Lot C	0.80 ± 0.14 (9)	1.30 ± 0.53 (5)
Lot D	0.80 ± 0.15 (4)	1.2 (1)

[a] Ratio of the sunlight photolysis rate constant to that observed for the photooxidation in Aucilla River water. [b] All solutions optically matched by adjusting absorbance to 0.20 (1.00 cm cell) at 366 nm. [c] Number of experiments in parentheses; each experiment involved triplicate kinetic runs for each solution. [d] Half-life in Aucilla River water ranged from about 20 minutes in winter to 5 to 10 minutes during summer at midday. [e] Half-life ranged from about 5 hours of midday sunlight during summer to 12 hours during winter. [f] Isolated from soils. [g] Obtained commercially.

ultraviolet (uv) and visible spectral regions (Figure 6). The humic substances in the river water water were nuch more effective in the middle uv, however. The wavelength dependence for the reaction (300-500 nm) in Aucilla River water can be described by Eq. 2 where X_{s,λ_o} is the response funcition at wavelength λ_o and λ is in nanometers.

$$X_{s,\lambda} = X_{s,\lambda_o} e^{0.023(\lambda_o - \lambda)} \qquad (2)$$

Employing computer generated values for near-surface solar spectral irradiance $E_0(\lambda,0)$ (2) and Eq. 3, rate constants were computed for the photosensitized oxygenation of DMF in sunlight using Eq. 3 (Figure 7) (8):

$$k_{s,\lambda} = E_o(\lambda,0)\ X_{s,\lambda} \tag{3}$$

The computations indicate that solar uv light is most effective at promoting reaction sensitized by humic substances in the river water whereas blue light is most effective in the case of the humic acids. The computer was also used to integrate $k_{S,\lambda}$ over all wavelengths to obtain sunlight rate constants k_λ. The computed values indicate that near-surface half-lives for the DMF reaction should be 5 to 10 minutes at midday during summer at latitute 40 deg. N. These findings are in close agreement with experimental values (Table 1).

In addition to the studies described above, other studies by Mill and coworkers (10) have indicated that alkoxy, alkylperoxy, and hydroxyl radicals are formed upon exposure of natural waters to sunlight. Such radicals may be derived from photolysis of peroxides that form as products of reactions between singlet oxygen and substances in the water. Mill and coworkers (10) used cumene (CUH) and pyricine (C_5H_5N) as probes to determine steady state concentrations of the radicals [$RO_2^{\bullet}$] and [$HO^{\bullet}$] in sunlight-exposed natural waters. Zepp and coworkers (6) computed steady-state concentrations of singlet oxygen in natural waters[$^1O_2$*] assuming [$^1O_2^*$] = k_S/k_A where k_S and k_A are sunlight rate constants (1-cm path length) for DMF oxygenation in the water and k_A is the bimolecular rate constant for reaction between DMF and singlet oxygen. Results of the studies by Mill and coworkers and Zepp and coworkers are summarized in Figure 8. Bimolecular rate constants for reactions between these

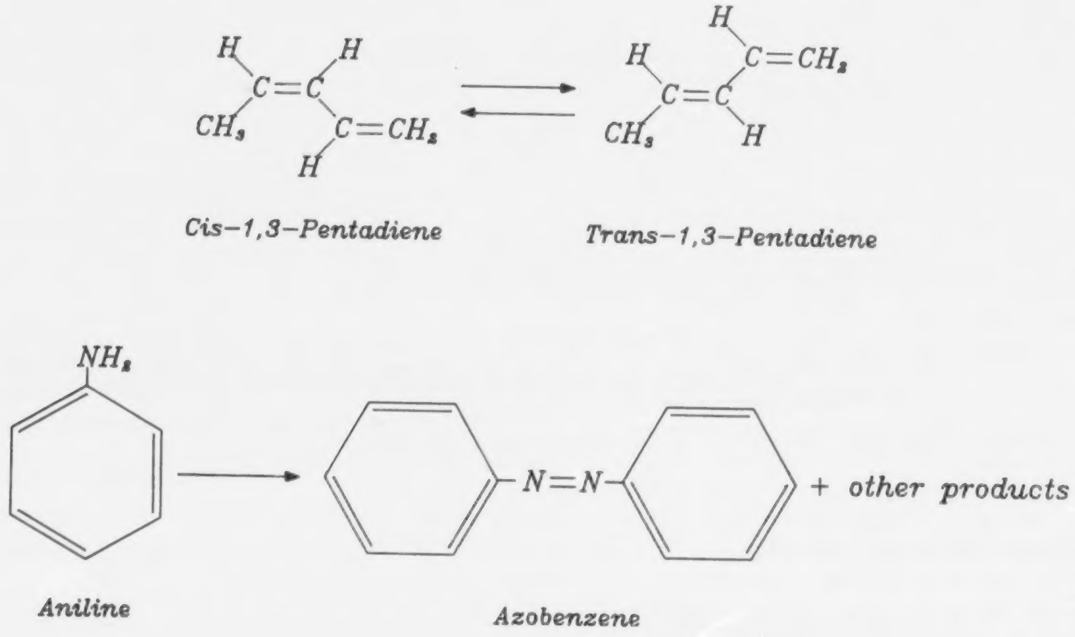


Figure 5. Reactions photosensitized by humic substances in water (7).

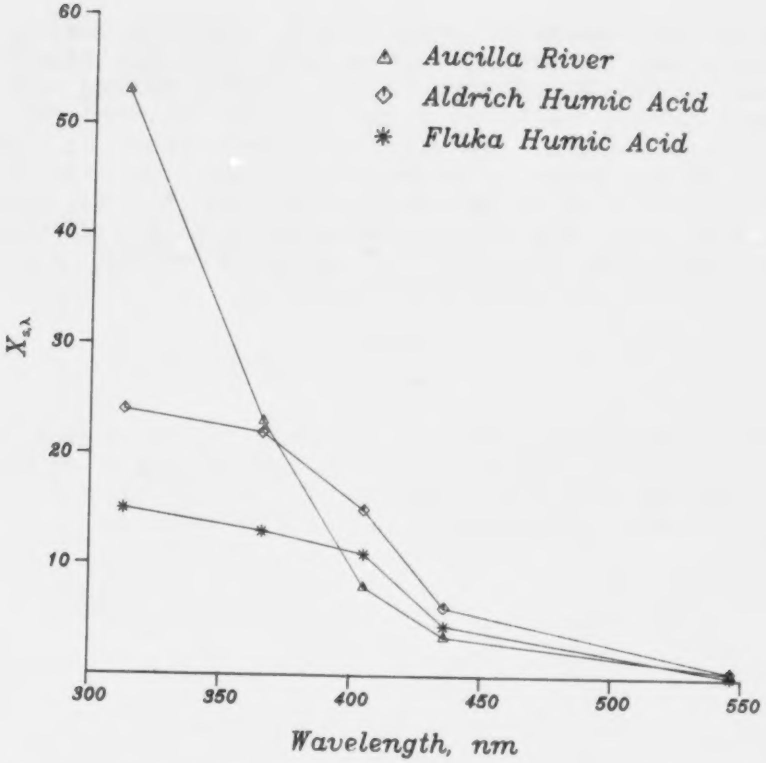


Figure 6. Action spectra for photosensitized oxygenation of 2,5-dimethylfuran. Reaction conditions: absorbance of each solution at 366 nm was adjusted to 0.20 in a 1.00-cm cell, pH was adjusted to 6.0 (8).

oxidizing species and various organic substrates are available in the chemical literature. These can be used in conjunction with the data in Figure 8 to estimate near-surface rate constants for the sunlight-induced oxidation of pesticides in natural waters (6,10).

Light Attenuation

To calculate photolysis rates of pesticides or other photochemical of photobiological processes in aquatic ecosystems, it is necessary to quantitate the penetration of the photochemically active uv and visible wavelengths of sunlight. The solar spectral irradiance just beneath the air-water interface of a water body $E_0(\lambda,0)$ is attenuated by dissolved and suspended matter as it penetrates downward. The irradiance is attenuated approximately in exponential fashion; that is, irradiance at depth Z, $E_0(\lambda,Z)$, is approximately $E\ (\lambda,0)e^{-K_T(\lambda)Z}$. The constant $K_T(\lambda)$, the diffuse attenuation coefficient) is the focal point of efforts to predictively model light attenuation in natural waters (11,12).

Smith, Baker, and coworkers have measured the penetration of sunlight into a variety of natural waters. They have used the experimental measurements to develop a model for sea water that partitions the diffuse attenuation coefficient into various components responsible for total attenuation (13, 14). This model assumes that the primary species responsible for attenuation in sea water are water itself, chlorophyll-like pigments derived from algae, and dissolved organic matter; the latter is particularly important for attenuation of uv light in coastal waters. The dissolved organic matter is referred to as humic substances in this paper, although oceanographers refer to it as "yellow substance" (12). Studies of Miller and Zepp (15) indicate that suspended sediments also play a key role in the attenuation of solar radiation in freshwaters. These studies are discussed in a subsequent section. A general equation for $K_T(\lambda)$ in natural waters is:

$$K_T(\lambda) = K_w(\lambda) + K_c(\lambda) + K_h(\lambda) + K_s(\lambda) \tag{4}$$

where $K_w(\lambda)$, $K_c(\lambda)$, $K_h(\lambda)$ and $K_s(\lambda)$ are components of the attenuation coefficient attributable to water, chlorophyll, humic substances and sediment, respectively. Equations and coefficients required for the calculation of $K_w(\lambda)$ and $K_c(\lambda)$ are discussed fully elsewhere by Smith and Baker (13,14).

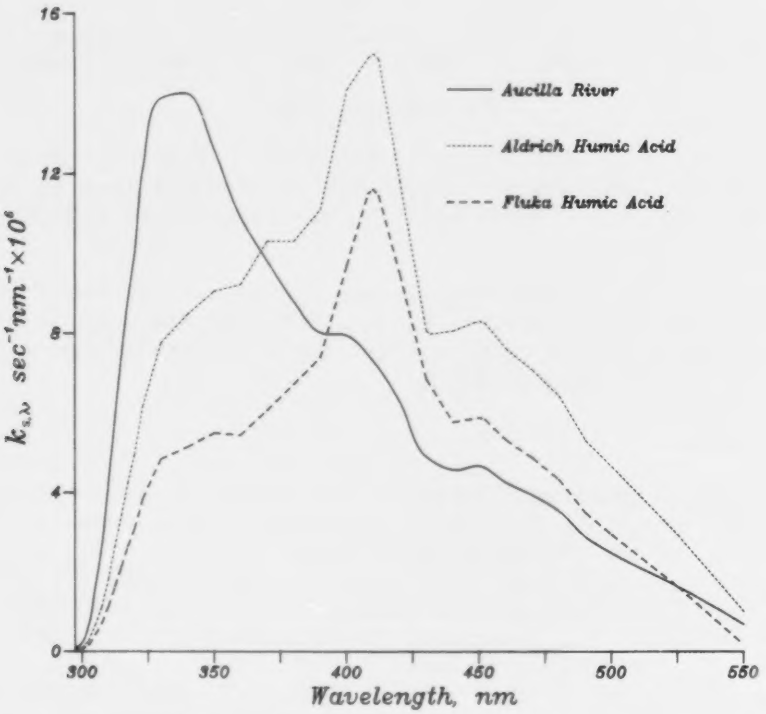


Figure 7. Wavelength dependence of rate constants computed for photosensitized reaction of 2,5-dimethylfuran in sunlight (midday, summer, latitude 40 deg. N). Rate constants, k_S , integrated over the entire spectral region are: Aucilla River, 5.4 hr^{-1}; Aldrich humic acid, 6.5 hr^{-1}; Fluka humic acid, 4.3 hr^{-1} (8).

WATER	PROBE	OXIDIZING SPECIES CONCENTRATION (M)		
		$[{}^1O_2^*] \times 10^{12}$	$[RO_2\cdot] \times 10^9$	$[HO\cdot] \times 10^{17}$
AUCILLA RIVER, FL	DMF	1.8		
	CUH		2.8	1.8
GULF OF MEXICO, FL	DMF	0.3		
MISSISSIPPI RIVER, LA	DMF	0.5		
COYOTE CREEK, CA	CUH		9.1	1.6
	C_5H_5N		5.0	

Figure 8. Near-surface steady-state concentrations of oxidizing species in natural water samples exposed to sunlight (6,10).

As interest in the effects of solar uv radiation in aquatic ecosystems has intensified in recent years, so have efforts to quantitate the spectroscopic properties of humic substances. Recent papers by Bricaud and coworkers (17), Højerslev (18), Baker and Smith (14), and Zepp and Schlotzhauer (19) have presented evidence that the humic substances in sea waters and freshwaters have closely similar spectral properties. Zepp and Schlotzhauer computed specific absorption coefficients $k_h(\lambda)$ for humic substances present in natural waters and extracted from soils (12):

$$k_h(\lambda) = \frac{2.303\, A_\lambda}{C_h\, l} = \frac{a_{h,\lambda}}{C_h} \qquad (5)$$

where A_λ = absorbance at wavelength

C_h = concentration of dissolved organic matter (humic substance) in mg organic carbon/liter

l = cell pathlength in meters

$a_{h,\lambda}$ = absorption coefficient of solution

Similarities in specific absorption coefficients were found for humic substances in soils and natural waters form the US and the USSR (Table 2, Figure 9). As originally reported by Jerlov (12), the decrease in k (λ) with increasing wavelength is exponential (Eq. 6):

$$k_h(\lambda) = Ae^{B(450-\lambda)} \qquad (6)$$

Table 2. SPECIFIC ABSORPTION COEFFICIENTS, k_h, FOR DISSOLVED HUMIC ACIDS AT pH 11 AND 465 nm (Ref. 19)

Source of Organic Carbon	k_h, $l(\text{mg Org. C})^{-1}m^{-1}$
Fluka Humic Acid	1.8
Aldrich Humic Acid	1.9
Karl Roth Humic Acid	2.4
Fulvic Acid - CA Soil	1.1
Aucilla River, Lamont, FL	0.70
Humic Acid - Sod Podzolic[a]	0.92
Humic Acid - Gray Forest[a]	2.46
Humic Acid - Ordinary Chernozem[a]	2.51
Humic Acid - Meadow Solonetz[a]	1.70
Humic Acid - Serozem[a]	1.84
Humic Acid - Brown Mountain Forest[a]	1.50
Humic Acid - Mountain Meadow[a]	2.21
Humic Acid - Shallow Red Soil[a]	1.91
Humic Acid - Cinnamon Brown Soil[a]	1.40

[a] Data of Orlov concerning humic acids from Soviet soils (20).

Zepp and Schlotzhauer (19) determined values of A and B for a variety of humic substances (Table 3) and found that, for humic substances in natural waters and for soil-derived fulvic acids, mean values of A and B were 0.6 and 0.014, respectively, with wavelength λ in nanometers. Remarkably, both Højerslev (18) and Bricaud and coworkers (17) also found mean values of 0.014 for B when Eq. 6 was applied to their spectral data for humic substances in various parts of the sea. Assuming that additional studies confirm the generality of Eq. 6, the component of the diffuse attenuation coefficient attributable to humic substances $K_h(\lambda)$ can be computed using Eq. 7 where the distribution function D (11) equals about 1.2 in the uv region (2,18).

$$K_h(\lambda) = D\, k_h(\lambda)\, C_h \tag{7}$$

The data in Table 2 indicate that the mean value for the absorption coefficients $a_{h,450}$ of natural waters at 450 nm equals 0.6 meter^{-1} when C is 1 mg organic carbon/liter. Thus Eq. 7 also can be expressed as:

$$K_h(\lambda) = 1.2\ a_{h,450}\ e^{0.014\ (450-\lambda)} \qquad (8)$$

This equation may be employed in computations of the depth dependence of direct and indirect photolysis rates of pesticides in various types of natural waters.

Influence of Suspended Sediments

Photoreactivity of Chemicals Sorbed to Sediments

Hydrophobic pesticides in aquatic environments are known to partition to the clay and silt-sized particles collectively referred to as "suspended sediments." Several recent studies have examined the photoreactivity of nonpolar organic chemicals in aqueous suspensions of natural sediments (15,21-23).

Oliver and coworkers (21) investigated the possibility that photolysis rates of sorbed or dissolved organic chemicals may be enhanced by indirect photoreactions. Aqueous suspensions of several common clay minerals and a semiconductor powder, TiO_2, were exposed to uv radiation in the presence of free radical scavengers that were dissolved in the system. Results of the experiments indicated that only TiO_2 produced free radicals upon irradiation.

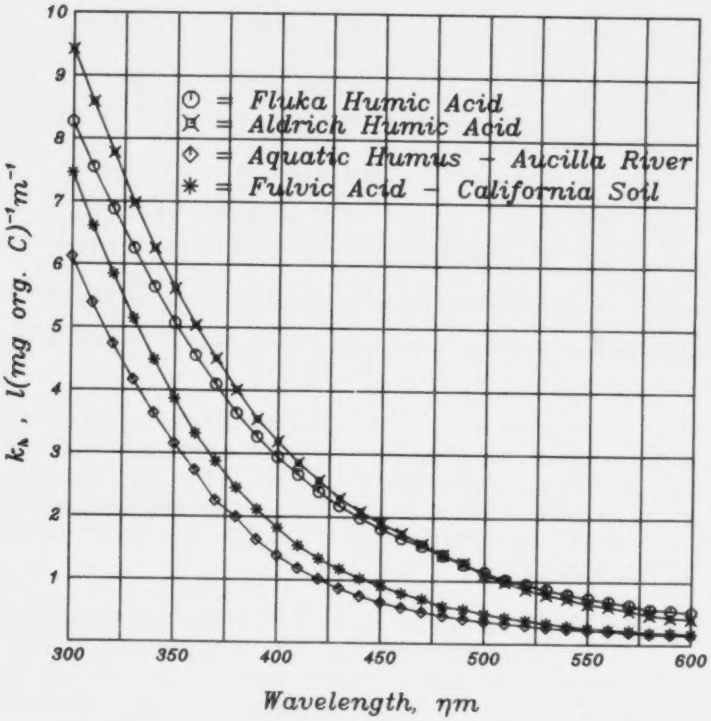


Figure 9. Electronic absorption spectra of various humic substances dissolved in water at pH 6.0 (19).

Table 3. PARAMETERS THAT APPLY TO COMPUTATION OF SPECTRAL VALUES OF SPECIFIC ABSORPTION COEFFICIENTS FOR VARIOUS HUMIC SUBSTANCES, k_h, WHERE $k_h = Ae^{B(450-\lambda)}$ liter (mg Org. C)$^{-1}$m^{-1}(λ is the wavelength in nanometers) (Ref. 19)

Source of Humic Material	pH	B	A	r^2 (No. of Values)
Fluka humic acid	6.0	0.0100	1.86	0.993 (31)
Aldrich humic acid	6.0	0.0104	1.90	0.999 (31)
Roth humic acid	6.0	0.0104	1.52	0.999 (31)
Humic acid - mean values		0.0102±0.0002	1.76±0.21	
Fulvic Acid - NC Soil	6.0	0.0146	0.861	0.997 (31)
Fulvic Acid - CA Soil	6.0	0.0139	0.909	0.999 (31)
Contech Fulvic Acid	6.0	0.0128	0.623	0.996 (28)
Fulvic acid - mean values		0.0138±0.009	0.80±0.15	
Aucilla River, Lamont, FL	6.0	0.0147	0.680	0.999 (31)
Okefenokee Swamp, Waycross, GA	4.1	0.0145	0.634	0.999 (31)
Suwanee River, FL		0.0140	a	0.996 (31)
Fenholloway River, Foley, FL	7.7	0.0134	1.09	0.996 (31)
St. Marks River, St. Marks, FL	8.7	0.0116	0.780	0.998 (16)
Quincy Bog, Tilton, NH	5.2	0.0150	a	0.994 (31)
Williamson River, Klamath Agency, OR	6.6	0.0152	0.382	0.999 (31)
Ogeechee River, Savannah, GA	6.5	0.0175	a	0.996 (31)
Econfina River, Perry, FL	4.2	0.0152	0.702	0.998 (31)
Freshwater aquatic humus - mean values		0.0145±0.0017	0.71±0.26	
Gulf of Mexico, St. Marks, FL	8.1	0.0151	0.249	0.998 (16)
North Sea[b]	8.1	0.0140	0.42	
Gulf of Mexico, near Tampa, FL[c]		0.0149	a	0.952 (13)
Marine aquatic humus - mean values		0.0147±0.0006	0.33±.09	
All aquatic humus - mean values		0.0145±0.0014	0.60±0.28	

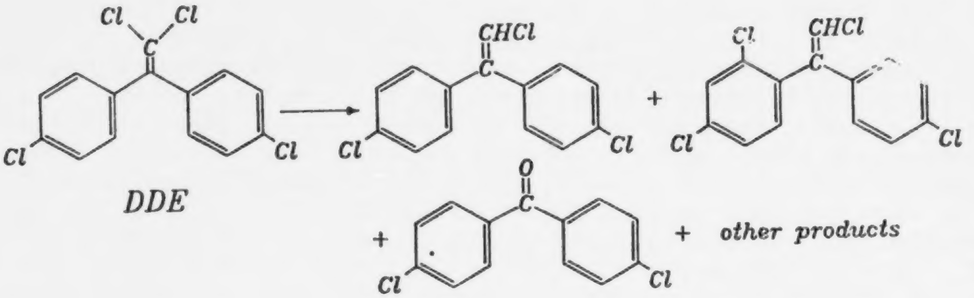
[a] Not determined.

[b] Computed from data of Højerslev (18) assuming yellow substance contains 50% by weight of organic carbon.

[c] Computed from diffuse attenuation coefficients (320 to 380 nm) for Gulf of Mexico near Tampa (14).

Additional studies indicated that TiO_2 photocatalyzed the decomposition of p-dichlorobenzene in water through an indirect photoprocess but that various clays and natural sediments were ineffective. Finally, it was shown that photolysis of methoxychlor (300 nm) was slower in the presence of suspended sediments than in distilled water. The slowdown was attributed to light attenuation by the sediments.

Miller and Zepp (22) compared the photolysis rates and products of four organic chemicals at trace concentrations in suspensions of natural sediments obtained from water bodies of the United States. The kinetic data were analyzed to disentangle the effects of light attenuation and scattering from the influence of sorption upon photoreactivity of the chemicals. The photoreactivities of the DDT metabolite DDE and the phenyl ketone, m-trifluoromethylpentadecanophenone, were found to be different in the sorbed state than in water, increasing with DDE bur decreasing with the ketone. Product studies indicated that the sorbed chemicals were in a microenvironment that is a considerably better hydrogen donor than water. Major products derived from photolysis of DDE sorbed on sediments are shown below:



(9)

The studies discussed above were conducted after equilibrating the suspensions for short time periods, usually less than one day, prior to irradiation. Pesticides that are resistant to biodegradation or hydrolysis, however, may remain sorbed in soil or bottom sediments for a long time prior to introduction into the water column of water bodies by runoff or resuspension. Zepp and Schlotzhauer (23) have reported that photolysis rates of DDE sorbed in aqueous sediment suspensions are affected by the length of time that the DDE is sorbed on the sediment (Figure 10). The terms Co and C in Figure 10 refer to the initial concentration of DDE in the suspension and the concentration after exposure to light, respectively.

The kinetic data for photolysis of sorbed DDE could be satisfactorily described by the model show in Eq. 10.

$$\begin{tikzcd} P \arrow[r, shift left, "X_r K_P"] \arrow[d, "k_w"'] & R \arrow[l, shift left] \arrow[r, shift left, "k_u"] \arrow[d, "k_s"'] & U \arrow[l, shift left, "k_{-u}"] \\ \text{Products} & \text{Products} & \end{tikzcd} \qquad (10)$$

This model, which is consistent with Karickhoff's interpretation of sorption kinetics (24), provides that the sorbed DDE, although predominantly photoreactive immediately after sorption, gradually diffuses into a microenvironment where the chemical is unreactive. The symbols p, R, and U represent concentrations of DDE dissolved in the aqueous phase, sorbed on the reactive part, and sorbed on the unreactive part, respectively. When the system is irradiated P and R rapidly photoreact, then photolysis becomes rate-limited by diffusion of DDE form the unreactive to the reactive environment. Kinetic parameters derived from analysis of the data (Table 4) indicate that: (1) after 60 days about half of the sorbed DDE was unreactive, (2) the DDE sorbed in the reactive part reacts at a higher rate than when it is dissolved in water, (3) at least 200 hours are required for one-half of the DDE sorbed in the unreactive part to diffuse into the reactive part. Karickhoff's work indicates that the magnitude of k_{-u} for various pesticides is likely to be inversely proportional to the sediment-water partition coefficient K_p (24).

Light Attenuation and Scattering by Suspended Sediments

The studies described in the preceding section all had one common finding: the predominant influence of suspended sediments was a reduction in photolysis rates caused by light attenuation. Basic principals involved in predictive modeling of light attenuation are discussed in an earlier section. Miller and Zepp (15) studied the photoreactions of several organic chemicals in sediment suspensions to obtain quantitative data concerning the effects of light attenuation and scattering by sediments on photolysis rates. Photolysis rates of the uv-sensitive (330 nm) actinometer, malachite green leucocyanide, were determined as a function of depth in aqueous sediment suspensions under sunlight. Diffuse attenuation coefficients, K_S, were computed from slopes of plots of the natural lorarithms of the photolysis rates of the actinometer versus depth in the suspensions. Specific attenuation coefficients, k_S, were computed by ratioing K_S to the sediment concentration (mg/liter) (Table 5).

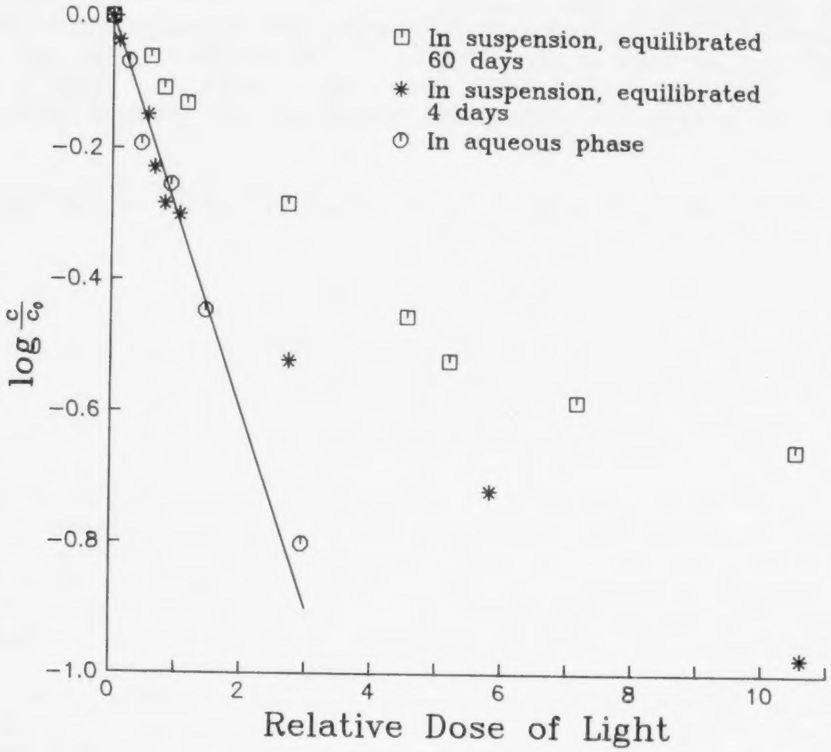


Figure 10. Photoreaction of DDE in aqueous suspension of Ohio River sediments (80 mg/liter) and in aqueous phase of the sediment suspension (23).

Table 4. KINETIC PARAMETERS DESCRIBING PHOTOREACTION OF SORBED DDE IN SEDIMENT SUSPENSIONS (Ref. 23)

Parameter	EPA-12	Sediment[a] EPA-26	EPA-13
$(X_r)_e$[b]	0.56	0.43	0.62
k_{-u}, hr^{-1}	5.8×10^{-3}	3.7×10^{-3}	4.7×10^{-3}
$(k_u + k_{-u})$, hr^{-1}	1.4×10^{-2}	6.3×10^{-3}	c
Light attenuation factor	0.33	0.30	c
60-day k_s/k_w	3.2	3.1	c

[a] Sediments obtained from an Ohio field (EPA-12), the Mississippi River (EPA-26), and the Ohio River (EPA-13).
[b] Fraction of sorbed DDE that was photoreactive after being sorbed for 60 days.
[c] Not determined.

Results indicated that k_s values fell in a surprisingly narrow range considering the diversity in the origin of the sediments.

Other experiments were conducted by Miller and Zepp (15) to ascertain the effects of light scattering on photolysis rates. The photoreaction of γ-methoxy-m-trifluoromethylbutyrophenone, MTB), (Figure 11), dissolved in various clay or sediment suspensions, was studied with Georgia sunlight as the light source. Under the reaction conditions the MTB was predominantly dissolved in the aqueous phase of the suspensions. Typical kinetic results with the clays are shown in Figure 12. The photolysis rate constant for MTB was actually enhanced in the presence of the uv-transparent clays. The enhancement was

Table 5. ATTENUATION COEFFICIENTS FOR SUSPENDED SEDIMENTS (Ref. 15)

Sediment	Concentration mg/l	K_s, cm^{-1}[a]	k_s, l mg^{-1} cm^{-1}[b]
Oconee River (GA)	82 ± 6	0.35	$4.8 \pm 0.5 \times 10^{-3}$
USDA Pond (GA)	17 ± 5	0.14	$8.2 \pm 3.0 \times 10^{-3}$
Hickory Hill Pond (GA)	44 ± 12	0.34	$7.7 \pm 2.5 \times 10^{-3}$
Broad River (GA)	41 ± 6	0.16	$4.0 \pm 0.9 \times 10^{-3}$
Missouri River	100 ± 20	0.32	$3.2 \pm 0.6 \times 10^{-3}$
Mississippi River	106 ± 3	0.50	$4.7 \pm 0.5 \times 10^{-3}$

[a] Diffuse attenuation coefficient at greater than two optical depths.

[b] Specific attenuation coefficient due to sediment; average value $5.4 \pm 2.0 \times 10^{-3}$ l mg^{-1} cm^{-1}.

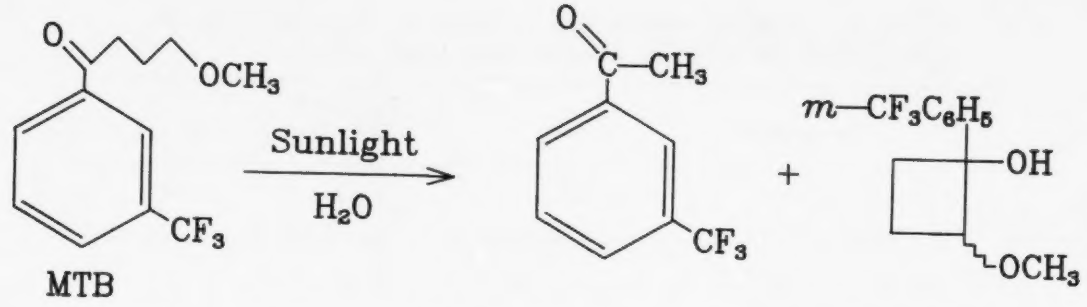


Figure 11. Photoreaction of γ-methoxy-m-trifluoromethylbutyrophenone (MTB) in sediment suspensions (15, 22, 23).

attributed to the increased pathlength of light caused by scattering by the clay particles. Light attenuation by the uv-absorbing kaolinite offset this increase at higher clay concentrations.

Smith and Fahy are presently conducting a more detailed study of the effects of sediments on penetration of uv and visible solar radiation into natural waters (25). These studies include experimental measurements of the transmission of solar spectral irradiance into sediment suspensions and development of equations that can be used to predict the light attenuation in unmeasured aquatic environments.

Effects of Microorganisms on Photolysis

Several investigations indicate that microorganisms, especially algae, may influence the photolysis rates of certain pesticides in the aquatic environment (26-30). That algae can mediate indirect photodegradation of certain chemicals is well established. For example, O'Kelley and Deason (27) presented data that established that the algal transformation of malathion proceeds much more rapidly in the presence of visible light than in the dark or in irradiated culture medium (Table 6). Cerniglia and Gibson (29) have found that blue-green algae can catalyze the hydrolylation of aromatic hydrocarbons.

Table 6. MALATHION DEGRADATION RATE CONSTANTS AND PESTICIDE HALF-LIVES FOR ILLUMINATED CULTURES (calculated as a pseudo-first-order process) (Ref. 27)

Organism	Replicate	k	Half-life, hr
[a]Chlorella (Isolate #1)	1	0.454	1.54
	2	0.241	2.89
[a]Anacystis nidulans	1	0.044	15.9
	2	0.064	10.8
Control (no algae)	1	0.006	116.4
	2	0.004	240.2

[a]Cell concentration 4 g wet weight/l of culture medium

Research is presently underway to examine the kinetics of light-induced microbial transformations. Several para-substituted derivatives of nitrobenzene, including methyl parathion, photoreacted more rapidly in distilled water containing green algae than in distilled water or in growth medium (Table 17). Nitrobenzene itself, however, was not susceptible to this effect. In all of these studies, controls established that no biodegradation occurred in the dark during the photolysis period. Because the studies were conducted at algae concentrations that are much higher than natural levels, additional experiments are required to assess the significance of these reactions.

Conclusions

The results described herein lead to the following major conclusions.

(1) Humic substances accelerate photolysis of pesticides in natural waters by photosensitizing several types of reactions, including oxygenations, isomerications of unsaturated compounds, and hydrogen transfer reactions. Rates of these reactions vary from one pesticide to another, but generally the reactions are most rapid in colored natural waters such as swamp water.

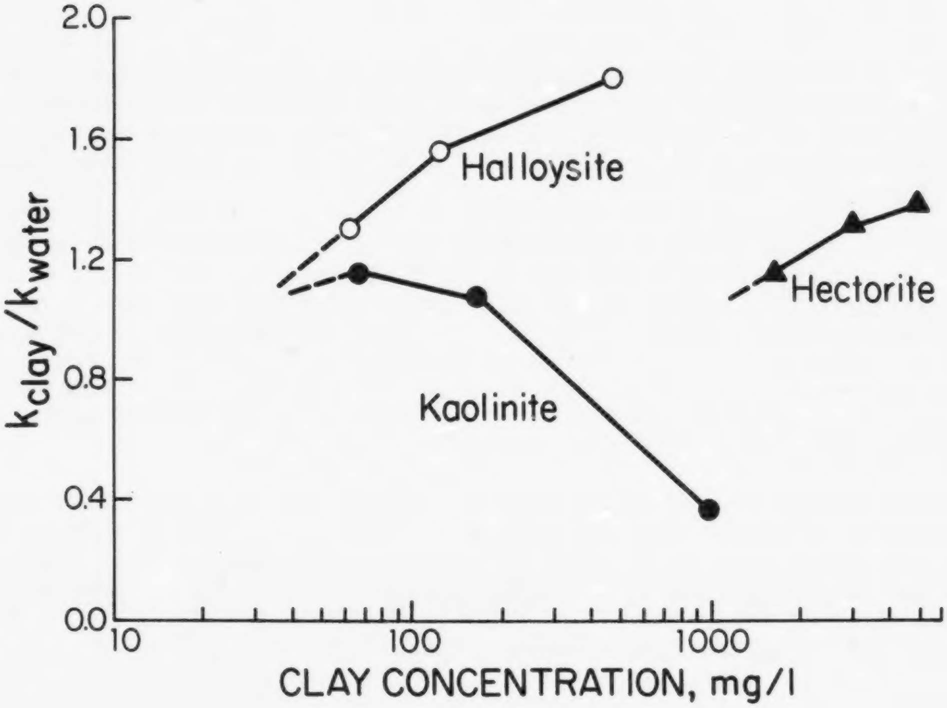


Figure 12. Effects of suspended clays on the photolysis of MTB; k_{clay} and k_{water} are first-order rate constants for photolysis in clay suspensions and in distilled water, respectively, at a depth of 2.9 cm under sunlight (15).

Table 7. EFFECTS OF THE GREEN ALGAE *Chlorella pyrenoidosa* ON LIGHT-INDUCED TRANSFORMATION OF VARIOUS CHEMICALS IN MAY SUNLIGHT (Ref. 30)

Chemical	Medium	Algae Conc. (g/l)	k_p, hr^{-1}
Methyl parathion	Distilled H_2O	0	0.01
	Distilled H_2O	0.79	0.30
	Distilled H_2O	0.15	0.09
	Benson-Fuller	0	0.05
	Benson-Fuller	0.57	0.19
	Benson-Fuller	0.057	0.09
p-Nitroanisole	Distilled H_2O	0	0.094
	Distilled H_2O	0.15	0.12
p-Nitroacetophenone	Distilled H_2O	0	<0.01
	Distilled H_2O	0.18	0.10
Nitrobenzene	Distilled H_2O	0	<0.02
	Distilled H_2O	0.15	<0.02
Aniline	Distilled H_2O	0	<0.005
	Distilled H_2O	0.18	0.03
Malathion	Benson-Fuller	0.57	0.05

(2) Photosensitizing and spectral properties of humic substances derived from diverse natural waters and soils fall in a remarkably narrow range. Humic substances in water bodies attenuate solar radiation most strongly and photosensitize oxygenations most rapidly in the uv and blue spectral region.

(3) The major effect of suspended sediments on photoreactions appears to be retardation attributable to light attenuation, and in the case of hydrophobic chemicals, to diffusion of the chemical into unreactive sorption sites. Light attenuation by suspended sediments in the main determinant of the penetration of photochemically active solar uv radiation into many inland surface waters. As with the humic substances, specific attenuation coefficients for sediments from diverse water bodies were found to be very similar.

These conclusions are based on very limited data, and additional research is required to determine their generality. Nonetheless, results such as the finding that absorption coefficients of complex humic substances in freshwater and the sea can be computed by a simple relation (Eq. 6) provide encouragement that prediction of the influence of natural substances on photolysis rates may not be as complicated as it originally seemed.

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APPROACHES TO THE STUDY ON THE KINETICS OF LIQUID-PHASE PESTICIDE TRANSFORMATION

by

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In the general case, the rate of chemical transformation of a pollutant in environmental objects is the sum of its transformation rates in various reaction channels which to a first approximation can be considered independent. In each of the channels the rate is a function of environmental parameters. Despite a great variety of factors determining the state of the environment, only some of them affect the rate of chemical detoxication of a pollutant in one or another reaction channel. A major purpose of laboratory research is to reveal possible transformation routes of a chemical and significant parameters as well as to establish a functional relationship between the effective rate constant and these parameters. In this case, two approaches are possible: either carry out studies on natural water samples and find statistical regularities; or study the mechanism of chemical transformation of a pollutant on the principle "from simple to complex", the latter approach being considered by us as a more productive one.

As an example, we have studied the mechanism of liquid-phase transformation of 3,4-dichloroaniline(DCA), an intermediate transformation product of amido-containing compounds. Data are presently available on the destruction of chlorinated anilines, mainly due to photochemical and microbiological processes, as well as on the overall characteristics of the DCA decomposition dynamics in some natural waters (I). On the other hand, information is almost lacking in literature on the kinetics and mechanism of DCA transformation in the dark, and on the photoinduced oxidation of DCA, with free radicals participating. And the processes mentioned can play an important part in the pollutant transformation under environmental conditions.

Studies on the kinetics of the process in the dark were carried out in isothermal regime using an installation with flowing gas and light-isolated reaction vessels. In these experiments, a contribution of evaporation to the observed rate of the process did not exceed 2%. Analytical control of DCA concentration was performed by spectrophotometry and gas chromatography. Kinetic analysis was carried out by the initial rates method.

Under natural conditions chemical processes occur, as a rule, at insignificant rates. Consequently, it is necessary to intensify chemical reactions in laboratory studies due to increased temperature and introduced additions of natural water components at concentrations exceeding their natural content.

In the general case, multicomponent natural water can be subdivided into a number of subsystems. The simplest of them is distilled water with regulated additions of various components of natural water. We considered a great number of such subsystems under both aerobic and anaerobic* conditions in the dark and with photoinitiation of radicals.

Additions of phosphate buffer to distilled water were found not to affect significantly the rate of DCA transformation. The rate of the reaction depends only slightly on pH of the medium over the pH range 5.3 to 8.8 and can be given by the first-order equation with respect to DCA concentration:

$$W_0 = -\frac{d[\Delta CA]}{d\tau} = k^{\bullet}_{eff}\,[\Delta CA] \qquad [I]$$

In the neutral medium at a temperature $25 \pm I\,^{\circ}$C, the effective rate constant K_{eff} is $(0.7 \pm 0.I)\cdot IO^{-6}$ s^{-I} and the effective activation energy is 6.5 ± I.0 Kcal·mol^{-I}·1 .

Low activation energy indicate that the process of DCA destruction under anaerobic conditions is associated with the presence of indigenous ions of transition metals. Ions of Fe(II,III) are known to be very abundant impurities. Their concentration can be as great as IOO mg·l^{-1} in natural waters and IO^{-6} mol·l^{-1} in distilled water. The assumption of a possible role of ferric ions was tested by sets of experiments where, on the one hand, we varied the concentration of Fe(III), and on the other hand, introduced sodium ethylene diamine tetraacetate(EDTA) converting ferric ions to a nonreactive form. As seen from Fig.I, the rate of the reaction is proportional to C_{Fe}. Extrapolation to zero rate corresponds to a content of indigenous ferric ions 2 to 3·IO^{-6} mol·l^{-1}. The same amount was found colorimetrically in the initial solution using α,α'-bipyridyl after the reduction of ferric ions by ascorbic acid additions.

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[*] Anaerobic conditions were establihed by purging argon through the solution. This technique,however,did not enable us to eliminate completely the traces of oxygen.Residual concentration of oxygen was about IO^{-6} mol·l^{-1}.

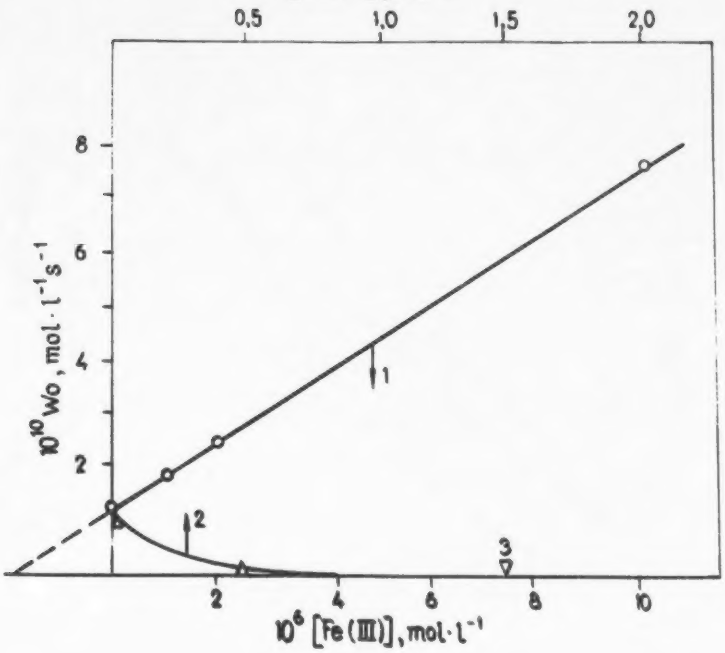

Fig.I. Dependence of the DCA oxidation rate on additions of ferric ions(I) and EDTA (2); 3 – DCA transformation in the presence of IO^{-5} mol·l^{-I} of Fe(III) and $I.5\cdot IO^{-4}$ mol·l^{-I} of EDTA. t = 70°C, $[DCA]_0 = 5\cdot IO^{-5}$ mol·l^{-I}, pH = 7, [phosphate] = $6.7\cdot IO^{-2}$ mol·l^{-I}. Experiments were carried out at the atmosphere of argon with a small addition of oxygen at a content of indigenous ferric ions in the solution of $2\cdot IO^{-6}$ mol·l^{-1}. Arrows show the corresponding abscissas.

Introduction of EDTA into the system completely inhibits the process (Fig.I). Thus, the main route of chemical transformation of DCA in distilled water is not hydrolysis but its oxidation by indigenous ferric ions likely to be present in water in the form of microcolloid hydroxide. Apparently, one should take into account a possible role of ferric ions, when analyzing the influence of other factors, such as the content in water of hydrogen peroxide and ligands of organic and inorganic origin, exposure to sunlight, etc.

Considering the obtained data on the oxidative character of DCA destruction by ferric ions, it is interesting to study the influence of ions of copper and other heavy metals. As seen from Fig.2 (curve I), the rate of DCA transformation depends

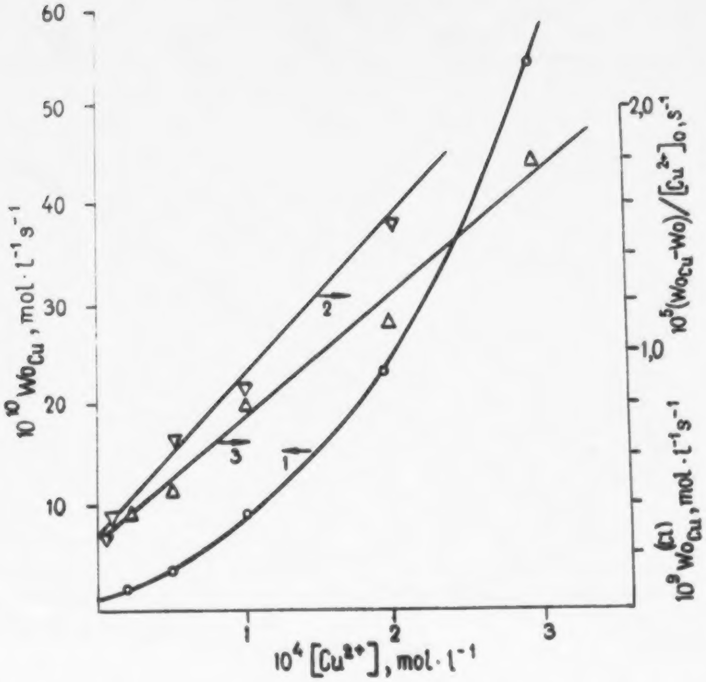

Fig.2. Dependence of the DCA oxidation rate on additions of Cu(II) ions in the absence of $W_{0,Cu}$ (I) and in the presence of 0.5 mol·l⁻¹ NaCl ($W_{0,Cu}^{Cl}$ (2); 3 - linear anomorphosis of curve(I): $(W_{0,Cu} - W_0)/[Cu^{2+}] = 2.5 \cdot 10^{-6} + 5 \cdot 10^{-2}[Cu^{2+}]$, where W_0 is the background reaction rate without Cu(II) additions. I - $[DCA]_0 = 5 \cdot 10^{-5}$ mol·l⁻¹, 2 - $[DCA]_0 = 3 \cdot 10^{-5}$ mol·l⁻¹, pH=7, t = 70°C, [phosphate] = $6.7 \cdot 10^{-2}$ mol·l⁻¹. Conditions are close to anaerobic ones (argon with a small admixture of O_2). Arrows show the corresponding ordinates.

quadratically on the content of Cu(II) ions. Along with the one-electron channel, the contribution of which is characterized by a section cut off by a linear anamorphosis(Fig.2, curve 3) on the ordinate, the two-electron channel is realized due to the cooperation of two Cu(II) ions in an elementary act of DCA oxidation.

Experiments with additions of cations of manganese(II), vanadium(V) and mercury(II) at concentrations to 10^{-6} mol·l⁻¹ did not reveal the influence of these ions on the rate of DCA oxidation.

In addition to the ions of polyvalent metals, the rate of substrate transformation can be influenced by various anions and organic compounds present in natural waters. This influence can show itself as the change in concentration and composition of the coordination sphere of soluble forms of transition metal ions; formation of donor-acceptor complexes with the substrate; and interaction with intermediate free radicals.

We varied the concentrations of anions Cl^-, NO_3^-, SO_4^{2-} and CO_3^{2-} from 0 to 4.0 $mol\cdot l^{-1}$ for Cl^- and to $IO^{-2}\ mol\cdot l^{-1}$ for the others. The chosen interval of concentrations overlaps the range of possible levels of these nucleophiles in natural water bodies. Additions of chloride-ions were found to result in increased rate of the process.

It is interesting that in the presence of 0.5 $mol\cdot l^{-I}$ chloride-ions the order of the reaction with respect to Cu(II) concentration becomes first(Fig.2,curve 2). This fact appears to be associated with increased redox potential of Cu(II) during the formation of chlor-aquacomplexes, resulting in increased contribution of the one-electron channel.

Varying the concentration of sodium sulfate to $IO^{-2} mol\cdot l^{-I}$ and sodium iodide to $IO^{-4}\ mol\cdot l^{-1}$ did not affect significantly the rate of DCA transformation,whereas additions of nitrate-ions had a pronounced inhibiting effect. Dependence of the initial rate of DCA oxidation on the concentration of nitrate-ions is given by hyperbolic function. Similar character of the dependence was also observed in the presence of ferric ions at a concentration of $IO^{-5}\ mol\cdot l^{-1}$.

Organic compounds in natural waters are represented by a great variety of substances, among which are humic and fulvic acids tending to form donor-acceptor complexes and associates.

As humic acids were added to distilled water, the rate of the process was found to decrease, amounting to one half the initial rate even in the presence of 5 mg/l of humic acids. These results agree with the literature data,according to which iron converts from the microcolloidal state to a watersoluble complex with dissolved organic matter (DOM) in the presence of DOM of natural origin. It is likely that the polydentate character of this ligand sharply reduces the redox potential of ferric ions, thus acting similarly to EDTA.

Oxygen and the product of its two-electron reduction-hydrogen peroxide, are the most important environmental factors. Typical content of H_2O_2 in natural water bodies amounts to IO^{-6} - IO^{-5} $mol\cdot l^{-1}$ (2). In some cases,however, it can be even higher. Hydrogen peroxide is known to be an effective source of free radicals in the presence of metallic ions.

Under anaerobic conditions in the presence of hydrogen peroxide the rate of the reaction increases, as does the effective activation energy which amounts to (8.2 ± 0.8) $Kcal\cdot mol^{-1}$ in the neutral medium at a concentration $[H_2O_2] = 5\cdot IO^{-4} mol\cdot l^{-I}$. In the presence of H_2O_2, the first-order reaction with respect to substrate concentration remains, as well as the linear character of the process rate dependence on the content of Fe(III) ions. In this case, as in the absence of H_2O_2 additions, the background reaction rate corresponds to that in the presence of indigenous ferric ions in the initial solution at a concentration of

$(2.0 \pm 0.5) \cdot 10^{-6}$ mol·l^{-1}, irrespective of pH of the medium. This suggests a catalytic character of H_2O_2 interaction with DCA where ferric ions act as catalysts.

The character of $C_{H_2O_2}$ influence on the rate of DCA transformation is determined by pH of the medium and the content of metallic ions. At pH = 7.0 the rate of DCA oxidation is proportional to $C^{0.5}_{C_2H_2}$ that is indicative of the chain mechanism of the process with a quadratic chain interruption. The chain mechanism can be realized due to the initiation of radicals, as ferric ions interact with both DCA and H_2O_2. The resulting ions of bivalent iron interact with H_2O_2 that leads to the occurrence of highly reactive radicals $\dot{O}H$ in the system.

At high concentrations of hydrogen peroxide, radical OH interacts with H_2O_2 to form superoxide radicals (O_2^-) in the system. As a result, a catalytic process of H_2O_2 decomposition to water and oxygen can be realized.

In the absence of competitive additions and at relatively low concentrations of H_2O_2, radicals OH and O_2^- interact with DCA, and those of DCA formed in the system interact with ferric ions. Occurrence of the chain mechanism of DCA oxidation in the dark is evidenced by a decrease in the reaction rate, as ethanol which is a typical inhibitor of chain-radical reactions is introduced into the system (Fig.3). The rate decreases to the same value, irrespective of the initial concentration of H_2O_2, this value coinciding with the rate of DCA oxidation in the absence of H_2O_2 additions. In this case, the initiation of radicals is accomplished mainly through the interaction of ferric ions with DCA

$$Fe^{3+} + \Delta CA \rightarrow Fe^{2+} + \dot{R}, \qquad [2]$$

$$\dot{R} + Fe^{3+} \rightarrow Fe^{2+} + P, \qquad [3]$$

where P is the product of the two-electron channel of DCA oxidation.

When using copper ions as catalysts, one observes a linear increase in the rate of DCA oxidation, as the concentration of H_2O_2 and Cu(II) increases, suggesting the chain process.

In the presence of H_2O_2, the inhibiting character of the influence of nitrate-ion and humic acid additions remains. It is seen that the effect of these additions shows itself mainly at the stage of radical initiation. It is this stage that determines the rate of DCA transformation both in the absence and in the presence of H_2O_2 additions.

We have studied the dependence of the process rate on the concentration of oxygen in the absence of H_2O_2 additions. The experiments were carried out in an atmosphere of pure oxygen and its mixtures with argon. The influence of oxygen on the

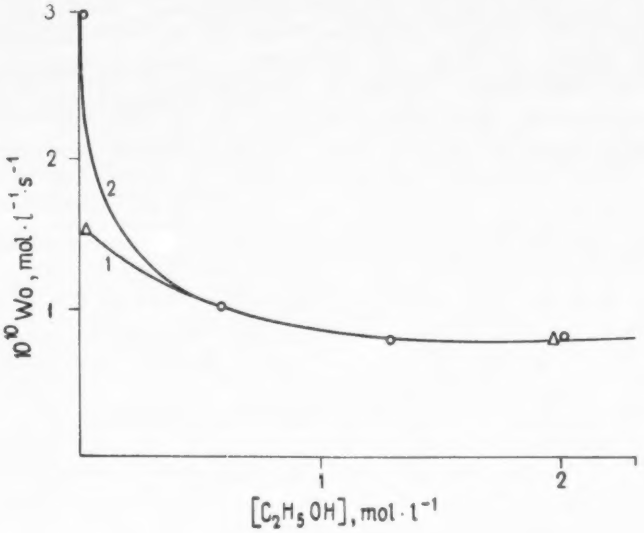

Fig.3. Influence of ethanol additions on the rate of DCA oxidation in the absence (I) and in the presence(2) of IO^{-3} mol·l^{-1} H_2O_2. Conditions are close to anaerobic ones (barbotage of the system with argon and a small admixture of O_2). $[DCA]_0 = 6 \cdot IO^{-5}$ mol·l^{-1}, pH = 7, [phosphate] = $6.7 \cdot IO^{-2}$ mol·l^{-1}, t = 70°C.

process rate turned out to be much the same in its character as that of hydrogen peroxide: the rate of DCA oxidation in the presence of oxygen increases, and depending on pH of the medium, the order of reaction with respect to C_{O_2} changes from zero (pH = 9.0) to first (pH = 4.0). The effective activation energy of DCA oxidation at pH = 7.0 was found to be about 6.0 Kcal·mol·l^{-1} irrespective of O_2 concentration.

At high concentrations of oxygen, radical of dichloroaniline formed in the stage of initiation interacts with O_2 to yield peroxide radical. Then the latter can either undergo recombination, or break down to form superoxide radical, or interact as an oxidant with other components of the system, such as DCA and ferric ions.

In a mixed oxygen-peroxide system, the rate of DCA transformation does not depend on pH of the medium over the pH range 5.3 to 8.8 and is proportional to the concentration of ferric and copper ions. Here, too, the inhibiting influence of nitrate-ions and humic acids remains. The order of the reaction with respect to $C_{H_2O_2}$ is fractional, suggesting the chain mechanism of the process.

Thus, the data presented indicate that the kinetics of DCA oxidation in aqueous solutions is determined by the interaction of this substrate with microimpurities of metallic ions. The influence of other components of water shows itself through a change in the content of active metallic form in the solution. Since the influence of these factors has an additive character, the expression for the overall rate of DCA transformation can be presented, depending on the significant parameters of natural waters for the process in the dark, in the form:

$$W=W_0\left(1+[M^{n+}]_{add}/[M^{n+}]_0\right)\frac{\left(1+[H_2O_2]^m\right)\left(1+[O_2]^n\right)}{\left(1+K_{NO_3^-}[NO_3^-]\right)\left(1+K_{DOM}[DOM]\right)} \qquad [4]$$

where W_0 is the background rate of reaction with indigenous ions of metals; $[M^{n+}]_{add}$ is the addition of ions of a transition metal M^{n+} ; and $[M^{n+}]_0$ is the background concentration of the same metal in water.

In this expression, the coefficients and order of the reaction with respect to the concentration of oxidants in the general case depend on pH of the medium. At pH 7.0 the order of the reaction with respect to O_2 and H_2O_2 is close to 0.5. Under these conditions, the initial rate of DCA oxidation measured experimentally in the simultaneous presence of varied additions is in satisfactory agreement with the rate calculated by equation [4]

The next stage of the work was studying the photochemical transformation of DCA and its oxidation by free radicals $\dot{O}H$ and $H\dot{O}_2(O_2^-)$. Photolysis was studied under anaerobic conditions in a thermostated quartz cell under the action of filtered light produced by a mercury-vapor lamp ДПШ -1000. Additions of H_2O_2 were used to generate free radicals. In this case, the rate of O_2 absorption or liberation was measured.

In agreement with the data presented in (3) , we found that under irradiation of DCA solutions with light at a wavelength λ = 313 nm there occurs photoinduced hydrolysis yielding 2-chloro-5-aminophenol. In this case, no radicals of the substrate are formed, since oxygen and additions of ascorbic acid acting as acceptors of free radicals do not affect the rate of the process. UV-irradiation of the DCA -H_2O_2 system leads to the effects of two types: photoinduced hydrolysis and oxidation of DCA at a rate equal to that of radical initiation during the photolytic decomposition of H_2O_2. It should be noted that under irradiation of DCA solutions with light at a wavelength of 313 nm a major contribution to the measured rate of the process is made by direct photolysis, whereas at a wavelength of 365 nm there occurs radical oxidation of DCA. In the absence of DCA, the rate of photochemical decomposition of H_2O_2 by the chain-radical mechanism is proportional to the square root of the light intensity, suggesting a quadratic chain interruption. In the presence of DCA, the rate of H_2O_2 decomposition is proportional to the value of light intensity and concentration of hydrogen peroxide to the first power, i.e. the chain interruption becomes linear. Consequently, DCA participates in the chain interruption.

Data on the inhibitory influence of DCA on the rate of H_2O_2 decomposition are given in Fig.4. Analysis of these data leads to a conclusion that at the stage of chain interruption DCA interacts with superoxide radicals. The rate constant of this reaction is about $3 \cdot IO^6$ $mol^{-1} \cdot l \cdot s^{-1}$ to an accuracy of one half the order of magnitude.

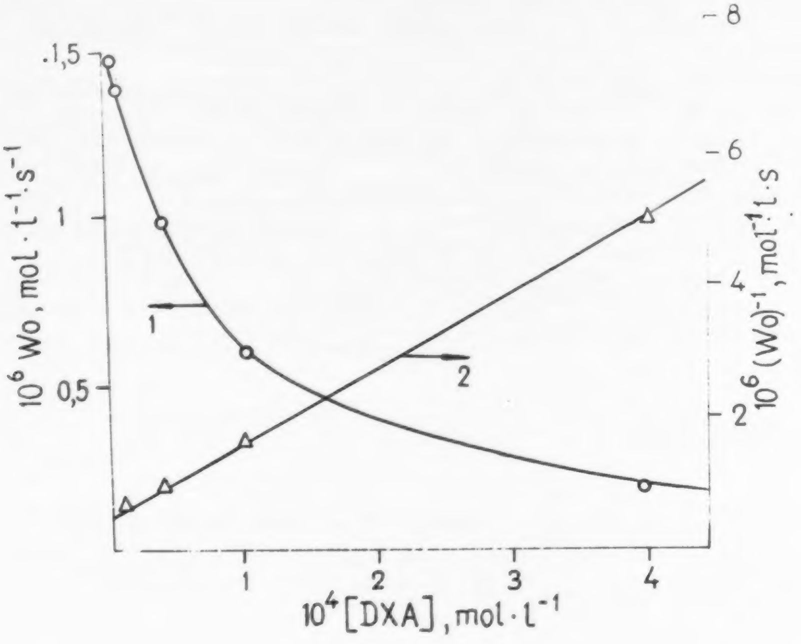

Fig.4. Dependence of the rate of O_2 release during the photolytic decomposition of H_2O_2 under the action of light (λ = 365 nm) on additions of DCA(I). λ = 365 nm. 2 - linear anamorphosis of curve (I). Arrows show the corresponding ordinates.

We have also studied the influence of various components of natural waters on the rate of photochemical transformation of DCA. In this paper we shall not consider these data. Just note that as a result of these studies it was concluded that there occurs no photosensitized reaction due to humic acids introduced to the solution at concentrations up to IO mg/l.

Based on the data obtained, it is possible to give some recommendations on the technique for extrapolating the results of laboratory measurements to natural conditions. The studies conducted showed that DCA has two major distinctive features:

relatively high quantum yield of direct photolysis and participation in oxidation-reduction transformations. Therefore, without considering microbiological processes, it is possible to select two main environmental parameters which determine the mechanism and rate of DCA transformation in natural waters. These are the intensity of insolation and the presence of oxidants and catalysts in a given natural water.

Effectiveness of direct photolysis depends on the absorbing capacity of natural water and the values of light scattering. Taking into account these factors is amenable to numerical modeling.

Oxidative properties of natural water,namely,the content of transition metallic ions(in particular,iron in the active form),hydrogen peroxide, and active intermediate particles, such as hydroxyl and superoxide radicals, depend on pH of the medium and the presence of iron and copper ions, as well as ligands and inhibitors in the solution. At present it does not seem possible to relate the oxidative capacity of water to any of the accepted parameters of natural waters. The purpose of further studies is to develop methods for determining concentrations of active intermediate particles under natural conditions.

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EFFECT OF SOME ECOFACTORS ON 3,4-DICHLOROANILINE DEGRADATION IN NATURAL WATER

by

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ABSTRACT

The studies are concentrated at 3,4-dichloroaniline (DCA) behavior in the modeled system "natural water". Disappearance of DCA (5 and 50 mg/l) from water is affected by physico-chemical and microbial processes. In the water based on a meadow-chernozemlike soil, transformation and degradation of DCA occur mostly under the action of facultatively-aerobic bacteria, all processes being accompanied by the DCA dechlorination. In the water based on a grey forest soil, the dominating factors in the pollutant disappearance are its absorption by organo-mineral colloids and chemical oxidation. Degradation of DCA is optimized by aeration and neutral or mildly alkali medium reaction (pH 7-8). When assessing the rate of natural water sources self-cleansing capacity in regard to DCA, the researcher has to take into consideration acidity of the medium, the content of dissolved oxygen and the ability of the population of saprophyte microorganisms to dechlorinate DCA in the process of its transformation.

Wide use of phenylamide herbicides in agriculture attracts special attention to 3,4-dichloroaniline (3,4-DCA), one of the most persistent and widespread products of their degradation. The paper deals with the studies of DCA microbial transformation in "natural water" and with the assessment of the effect of some ecofactors on the degradation rate. Two soils were selected as the study target: grey forest (GF) slightly loamy soil and meadow-chernozemlike (MC) moderately loamy soil with humus 2.1 and 3.9%, and pH_{water} 5.40 and 6.25, respectively. "Natural water" was prepared from the mixture of preliminary incubated soil (composted at 29°C) and distilled water (1:10). A top layer of suspension formed after a 24-hour settling was used in the experiment. The layer comprised colloid and subcolloid fractions of soil (4). The ratio of solid/liquid phases in GF/ and MC/natural water was 7:1000 and 16:1000, respectively. To maintain a required value of pH (5.5; 7.0; 8.0) phosphates of sodium and potassium were introduced into the medium. Glucose (0.01 and 0.1%) was used as an additional source of carbon supply. Erlenmeyer flasks (100 ml) were filled with 15 ml of the suspension. Then water solutions of DCA were added to form DCA concentration in the medium of the order of 5 and 50 mg/l. Incubation was carried out under steady-state conditions at 29°C in the dark. Oxygen supply was also varied (aeration by shaking).

Simultaneously DCA content was registered in the native and sterile versions of natural water. The samples were sterilized in an autoclave at 120°C and 1 atm overpressure. Content of DCA and its anilides in the suspension components was determined after centrifugal separation by gas-liquid chromatography and photometry (3). Concentration of chlorions was measured by potentiometric titration (2). DCA metabolites were recorded with the help of thin-layer chromatography. The quantity of saprophyte bacteria in natural water was determined by suspension inoculation in agarized medium No.1 composed according to our suggestion (1).

Following DCA introduction (5 and 50 mg/l) into MC-natural water, it is rapidly redistributed between liquid and solid phases. Dissolved and reversibly sorbed DCA extracted by an acetone-hexane mixture (9:1) gradually disappears from the suspension. DCA partition coefficient in the solid and liquid phases remains within 14.6±2.0. However, when the dissolved and reversibly sorbed DCA disappears the colloid fraction of soil suspension still retains up to 5-14% of the original chemical. It may be released only as a result of alkali hydrolysis under drastic conditions. This immobilized pollutant seems to be unavailable for microorganisms and unlike dissolved or reversibly sorbed DCA, is not degraded.

In the MC-natural water DCA disappearance consists of at least, two stages (Fig. 1). The first stage is slow disappearance of DCA comparable in rate to this process in sterile samples. The second stage is rapid disappearance of the pollutant accompanied by the release of chlor ions. Slow disappearance of DCA in the first stage (a lag period) is indicative of the adaptation of microorganisms to the substrate. Simultaneously there occurs a gradual accumulation of inducible enzymes participating in DCA destruction. In addition, at a DCA concentration of 50 mg/l the substrate itself and its metabolites, such as 4.5-dichloropyrocatecol, may show a bactericide effect. During this period one observes a fragmentary formation of

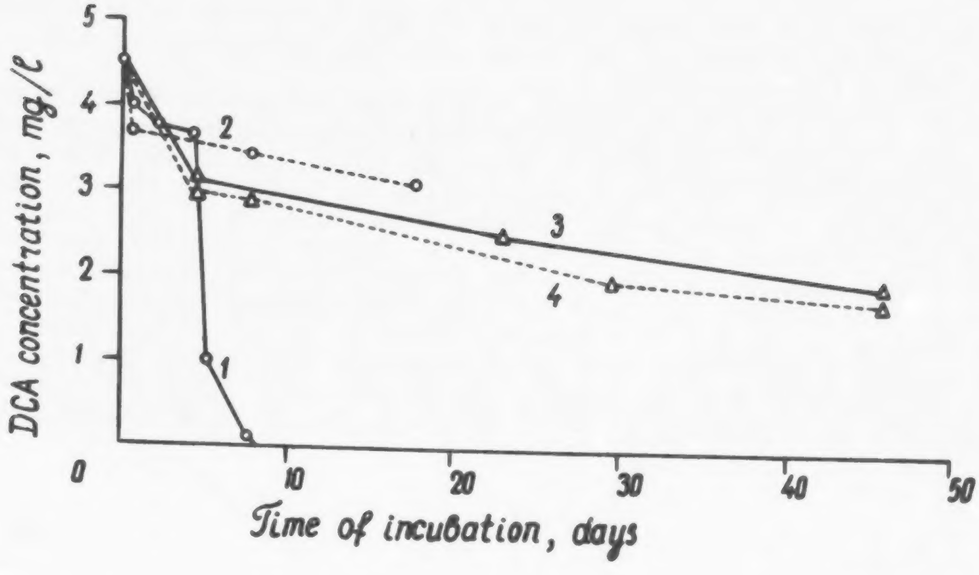

Fig.I. Dynamics of DCA disappearance (5 mg/l) from native (solid line) and sterile (dotted line) samples of MC-natural water(I,2), and GF-natural water(3,4).

various anilides (formanilide, acetanilide, propioanilide, butyranilide, etc), aminophenols and phenols. Depending on the DCA concentration (5 or 50 mg/l), the first stage may continue from two to twenty days.

When introducing DCA into the CF-natural water, the major part of the toxicant remains in the solution ($K_p = 9.8 \pm 0.2$), however, the aquatic systems under study differ from each other both in the toxicant behavior in them and in the content of saprophyte microorganisms (I3-22 and 22-38 mln cells in I ml of GF- or MC-natural water, respectively). In the native GF-natural water and its sterile version, DCA disappears slowly, apparently due to DCA binding to the organomineral colloids and further transformation under the effect of physico-chemical factors. After a four-month incubation of GF-natural water and DCA (5mg/l) the liquid phase produced I5% of the initial DCA. Fifty five percent of that amount was an immobilized form and could be extracted by a mixture of solutes or alkali hydrolysis. No release of inorganic chlor was recorded.

Bacteria inventory showed that DCA (5 mg/l) does not noticeably inhibit saprophyte growth in both natural waters. An increased dose of DCA (50 mg/l) in the MC-natural water leads to a slight decrease in the bacteria number. However, some time later this index reverts to the initial level. In time this coincides with the beginning of the second stage of DCA degradation. After a complete degradation of DCA a considerable increase in the saprophyte bacteria quantity is observed, particularly in case of an increased concentration of the chemical.

In the MC-natural water, DCA degradation was studied under the action of available carbohydrates,oxygen content and pH of the medium. At pH 7.0, glucose (0.0I and 0.I%) was found to increase the number of saprophytes by a factor of six and ten to forty,respectively. Slight acceleration of DCA degradation was observed only at increased concentration of glucose. Microorganisms using glucose as energy material do not apparently participate in the true DCA degradation. Buffering of the medium to pH 8.0 (in the presence of 0.0I% of glucose) leads to the double increase of saprophyte number on average,but does not show any significant acceleration of the DCA degradation rate as compared to pH 7 (Fig.2). In case of acidification

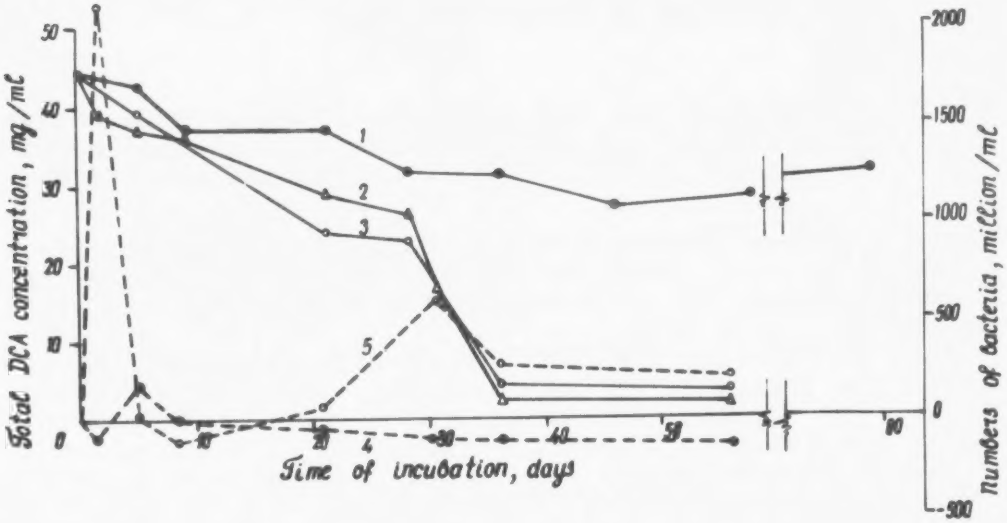

Fig.2. Dynamics of DCA (50 mg/l) disappearance from MC-natural water (with 0.0I% glucose) depending on acidity of the medium; I) pH 5.5 ; 2) pH 7.0; 3) pH 8.0. Influence of pH of the medium on saprophyte microflora: the number of bacteria reflects the difference between the version with pH 5.5 (4), pH 8.0 (5), and the version with pH 7.0; the initial content of saprophyte bacteria is 424.89 mln/ml.

of the medium (pH 5.5), the number of saprophyte bacteria drops I.5-2 times, and a significant slowing down of the DCA degradation rate is observed(Fig.2).

Aeration plays an important part in DCA degradation. Without the available air (in nitrogen atmosphere) DCA disappearance from water was slowed down and approached a sterile version (Fig.3). Additional aeration (shaking), though led to an increase in the number of microorganisms, did not influence the rate of pollutant disappearance.

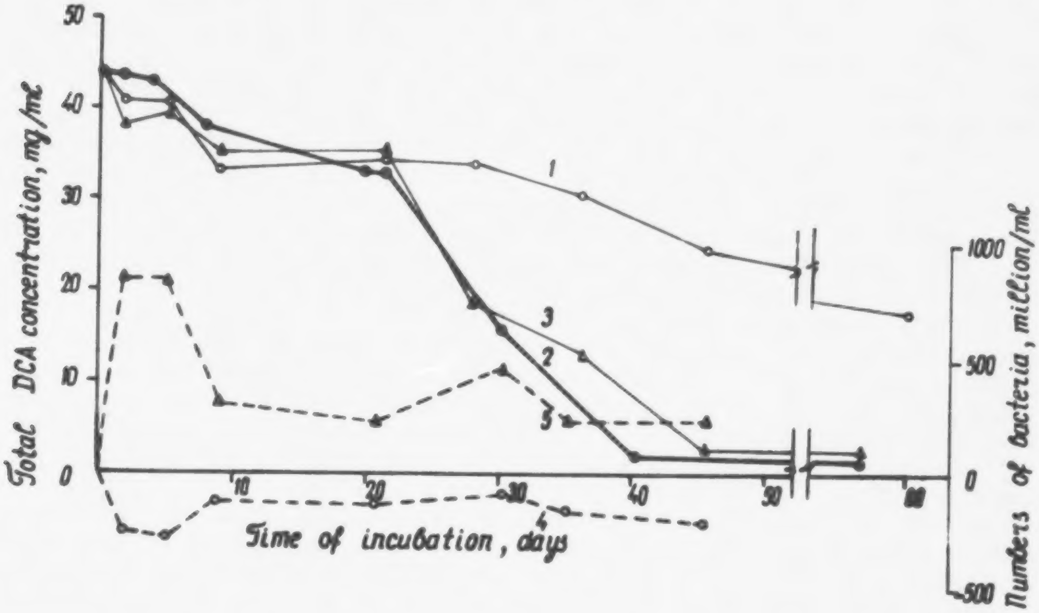

Fig.3. Dynamics of DCA (50 mg/l) diappearance from MC-natural water (with pH 7.0 and 0.0I% glucose) depending on oxygen supply of the medium: I) anaerobic conditions; 2) steady-state regime; 3) aeration by shaking. Influence of aeration on saprophyte microflora: number of bacteria shows the difference between the versions with anaerobic conditions (4); aeration (5), and a steady-state regime where the initial content of saprophyte bacteria is 424.89 mln/ml.

Thus, the degradation of the major part of DCA in the MC-natural water occurs under the effect of microorganisms, mainly facultatively-aerobic bacteria. This is confirmed by the drop of toxicant degradation rate in case of acidification of the medium and the absence of degradation under anaerobic conditions.

In the MC-natural water at pH 7-8 and in the presence of oxygen when dissolved and reversibly sorbed DCA disappears completely, over 60% of chlor ions of the maximum possible quantity are released independent of the glucose content. No accumulation of monochlorinated or unsubstituted anilines is observed in this case.This indicates that under the influence of certain species of bacteria there occurs cleavage of the aromatic ring and complete mineralization of the parent compound. Monochlorinated and unsubstituted compounds are known to be easily utilized by soil microflora, as a rule. One can suppose that DCA transformation in the MC-natural water follows the pathway of oxidizing deamination and cleavage of the ring of newly-formed chlorinated pyrocatechol, as it was found in the experiments on pure cultures. This also explains a significant increase in the number of saprophytes after the complete disappearance of DCA. The products of DCA intermediate metabolism apparently serve as a source of carbon supply for the microorganisms.

Slow disappearance of DCA from the GF-natural water unaccompanied by the release of chlor ions, may be explained by the absence in the soil of bacteria capable of transforming this compound. As the grey forest soil unlike meadow-chernozemlike one, has never been treated with phenylamide herbicides, the lag period during which a system of corresponding inducible enzymes is to be formed, is probably distinguished by a longer duration. The absence of direct correlation between the total amount of saprophyte bacteria in all the versions of the experiment on the natural water and the rate of DCA degradation indicates that only some definite group of saprophyte bacteria is responsible for the degradation and utilization of DCA.

Thus,

- disappearance of DCA in the natural water is determined by physico-chemical and microbial processes;
- in the water formed on meadow-chernozemlike soil, the main role in the DCA transformation and degradation is played by microbial processes which is confirmed by a release of chlor ions;
- in the natural water based on grey forest soil dominating factors in the pollutant disappearance are its absorption by the organo-mineral colloids and chemical transformations; the process of DCA disappearance is not accompanied by a release of chlor ions;
- pH 7-8 and aeration are the optimum factors for DCA degradation in the natural water, therefore pH and dissolved oxygen content should be determined to predict the rate of water source self-cleansing from DCA. Preliminary assessment of the capacity of natural microorganism population to dechlorinate substituted anilines in the process of their transformation is also important.

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TRANSPORT OF PESTICIDES AND RELATED CHEMICALS ACROSS AIR-WATER INTERFACES

by

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ABSTRACT

Anthropogenic chemicals including pesticides and related organic chemicals are transported in both directions across the interfaces of surface waters. Attempts at realistic prediction depend upon identifying the correct transport mechanisms and then using the appropriate thermodynamic and transport coefficients. From the standpoint of fate it is important to be able to treat vaporization and absorption from water surfaces; but it is equally important to consider all the sources and sinks associated with air-water interfaces. Those interfaces are: industrial wastewaters from manufacturing, wastewater treatment, the receiving streams, rivers, ponds, lakes and the oceans. Some of these interfaces can be sources and others can be sinks.

Pan evaporation treatment of woodtreating wastewater containing pentachlorophenol and naphthalene results in the volatilization of these chemicals into air. The rate equation is of the form:

$$N_A = N_W(x_a - x_a^*)$$

Where N is the flux rate of chemical A and water (W), x_a is the mole fraction of A in water and x_a^* is the mole fraction in equilibrium with A in the air. This equation has been verified for volatization of pesticides in the presence of high water evaporation rates. As the water evaporation rate decreases the more conventional rate equation, with N_W replaced with K_{A2}, the overall mass-transfer coefficient, may be used. The latter relationship has been verified for the case of methanol vaporizing from 7 to 110 acre ponds (1 acre = .4047ha).

The above rate equations are examples that reflect extremes in volatilization mechanisms. The ramifications of the natural environment also presents interface extremes and corresponding variability in air and water phase transport coefficients. This paper will review the existing body of transport science associated with the entire range of natural air and water interface processes, the availability of models, verification studies, important missing information and areas for possible research.

INTRODUCTION

Much is known about the physicochemical processes which control the movement of volatile substances across air-water interfaces. The volatile substances of concern include pesticides and a host of other man-made chemicals. Although the latter are not specifically applied to the natural environment they do find their way to this place. There is a continuing need to update and re-think existing models, validate existing models with field data and to fabricate new, more general models that will encompass all the variations in transport that exist in nature. As the desire for more realistic prediction methods develop highly sophisticated models will be needed. The new models will need to have time, position, and circumstance as independent variables.

It was sufficient in years past that air-water interface transport models had the capability of predicting order of magnitude flux rates, residence times, and compartmental concentrations in idealized ecosystems. (See Figure 1) This level of sophistication was considered adequate for general fate studies, screening of classes of chemicals for distribution, general aspects of hazard assesment and similar studies. In recent years there has arisen a need for a set of specific purpose transport models capable of making more precise predictions of rates, times, and concentrations.

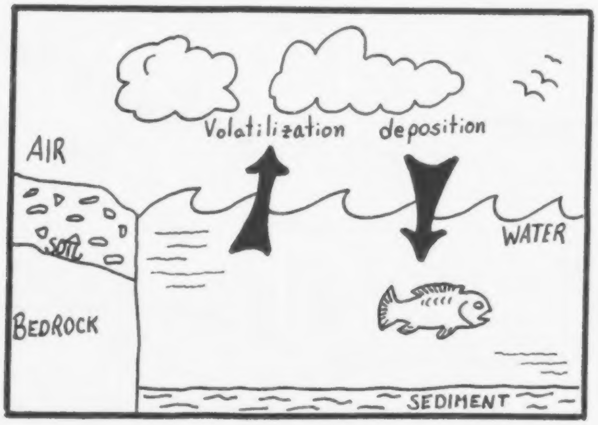

Figure 1. Chemical Volatilization from an Idealized Ecosystem.

Where the focus has been mainly on waterbodies, such as oceans and large lakes, it has now changed to include smaller portions of such bodies and also small lakes, rivers, streams and surface impoundments. The occurances of interest are accidental chemical spills on water, treatment, and storage of hazardous waste in impoundments, etc. With increasing frequency these occurances involve population centers where there is the need to assess the hazard in exposing humans and related biota to volatile chemicals. (See Figure 2) Somewhat apart from the emphasis and tack of the pesticide chemist there have been efforts by industrial chemists to build volatile chemical transport models that involve a broad spectrum of organic and inorganic chemicals. (See Table 1)

This paper will emphasize the general problem of volatilization of chemicals from water and to a degree the deposition onto water. The perspective will be that of an industrial chemist whose primary goal is to develop a set of models that apply to the near-field region of the

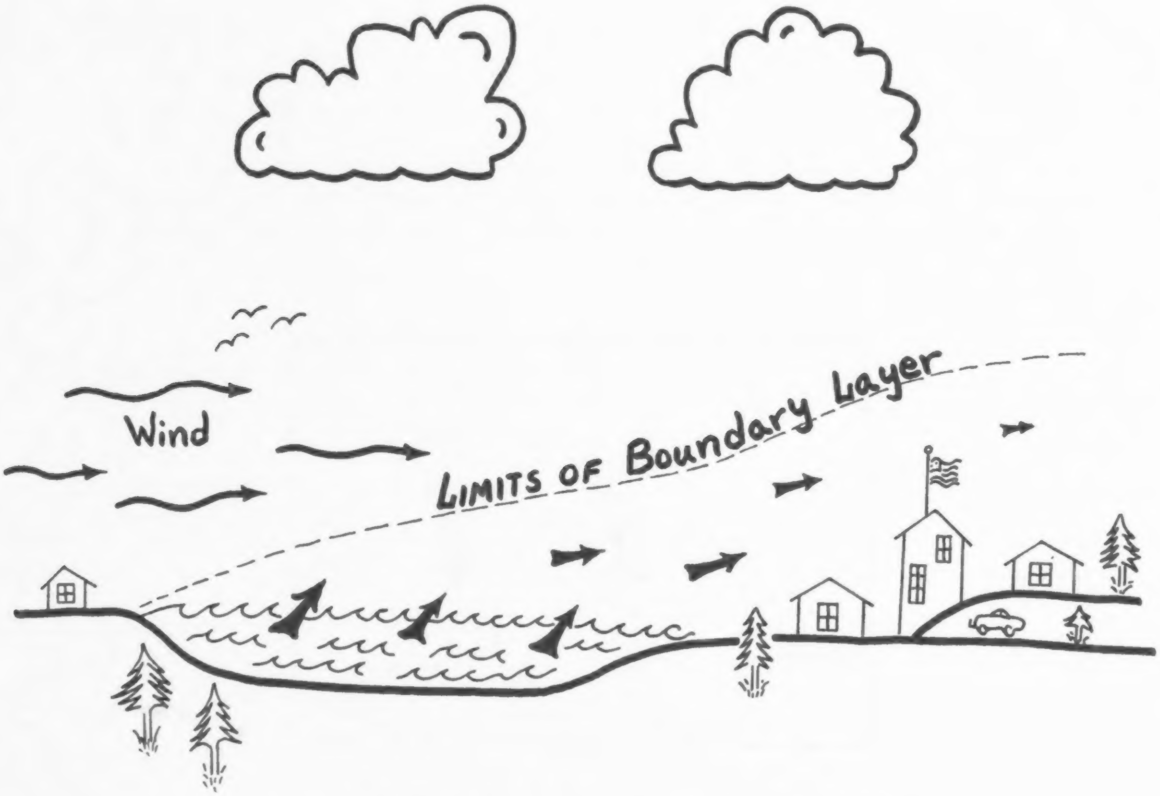

Figure 2. Volatilization and Exposure of Biota.

source. The sources in this case are operations associated with manufacture, transportation and disposal of chemicals. These sources are driven by natural processes such as wind and natural temperatures but are also driven by chemical process-type mechanical and thermal devices.

TABLE 1 BRIEF SCENARIOS OF CASES INVOLVING VOLATILIZING CHEMICALS FROM WATER SURFACES

PCB from the Hudson River the source of which are contamimated sediments

Chlorinated hydrocarbons from a harzardous waste storage impoundment

Odorous and nuisance substances from wastewater treatment basins.

Ammonia from a stream receiving ammonium nitrate

Miscible chemicals spilled in bulk quantities on water which have appreciable vapor pressures

Chemical slicks created from immiscible floaters which are pure or mixtures

BASIC PRINCIPLES AND SPECIAL CIRCUMSTANCE MODELS

Interphase transport principles find their basis in Fick's first and second laws of molecular diffusion. Failure of the molecular derived laws in the presence of turbulence has resulted in the use of a simple rate equation

$$N_A = K\Delta C_A \qquad (1)$$

which contains the parameter K which has been termed a mass transfer coefficient, turbulent transfer velocity, and chemical transport coefficient. In Equation 1, N_A is the flux of substance A in mol/cm^2.S, C_A is molar concentration of A in dilute solution in mol/cm^3 and K is the coefficient in cm/s. The complexity of arriving at realistic coefficients belies the simplicity of the equation. Employing a Fickian version of the flux equation with a turbulent diffusion coefficient equated to Equation 1

$$N_A = D^{(t)} \frac{\Delta C_A}{\Delta y} \simeq K\Delta C_A \qquad (2)$$

suggest that K may have inherited vectorial properties upon its creation since $\Delta C_A/\Delta y$ is a vector and $K \equiv D^{(t)}/\Delta y$. There seems to be ample theoretical basis to assume that K is dependent upon the direction of mass general principles and relations by which chemical vaporization (or absorption) rates can be obtained. Attention need be focused on the individual transfer coefficients for it is the proper selection of these values that will determine the realism of the calculated volatilization rate from the particular water surface circumstance.

Resistances in Parallel and Series

At the moment, there is little alternative but to use such models in attempts at determining sources and sinks of some substances on a global scale. In 1974, Liss and Slater[5] used this method to calculate the direction and flux of methane, carbontetrachloride, freon, methyl iodide, dimethyl sulfide, SO_2, N_2O and CO across the air-sea interface. In the calculation the average coefficients k_g (H_2O) = 3000 cm/hr and $k_l(CO_2)$ = 20 cm/hr were used in the resistances in series relation. That same year Thibodeaux and Parker[6] used the same general formulation to calculate emission rates of alcohols, aldehydes, acids and related organic residuals present in wastewater treatment. The wastewater basins varied in size from a few hectares to several hundred hectares. Mackay and Leinonen[7] also used the same method for estimating volatilization half-life from water of sixteen organic chemicals and metallic mercury. The organics included the pesticides DDT, lindane, dieldrin and aldrin.

In the case of the wastewater volatiles, the simple resistance in series idea was inadequate. Due to the placement of mechanical surface-water stirrers in the basins there were localized regions in which coefficients were enhanced and driven by altogether different mechanisms (see Figure 3). It was necessary to account for the parallel volatilization paths by

$$N_A = \left\{ \frac{A_n K_l^{(n)}}{A} + \frac{A_t K_l^{(t)}}{A} \right\} (C_A - C_A^*) \tag{5}$$

where $K_l^{(n)}$ and $K_l^{(t)}$ are overall coefficients that are characteristic of the natural and turbulent zones respectively, and where the total water-air interfacial area is $A = A_n + A_t$ which is made up of the natural area A_n and the turbulent area A_t.

The overall coefficients for each zone were obtained from Equation 3. However four individual coefficients were needed to characterize the localized transport mechanisms. The natural gas-phase coefficient was obtained from water evaporization studies performed on lakes since transport in this zone of the surface impoundment was not unlike that of lakes. The coefficient for water vapor is:

$$K_g^{(n)} = 11.8\ v_8/A_n^{1/20} \tag{6}$$

where v_8 is the wind speed at eight meters above the water surface in miles per hour (1 mi/hr = 0.447 m/s), A_n is in acres (1 acre = .4047ha)

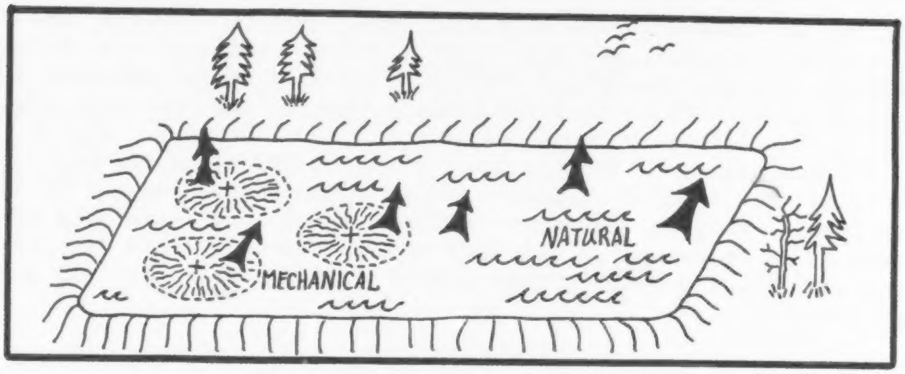

Figure 3. Mechanical Aerated Zones and Natural Zones of a Wastewater Treatment Surface Impoundment.

transfer. This aspect has particular application to employing measured values of chemical absorption coefficients in estimating desorption rates. The implied assumption is that the driving force, ΔC_A, accounts for the directional aspect.

The essence of the two-resistance theory for the interphase movement of chemicals was first proposed by Lewis and Whitman[1] in 1924. The film-theory for mass transfer was also in its prime at the time and to date the two-resistance theory is erroneously referred to as the two-film theory. The idea of resistances in series developed is designing an absorber for hydrogen chloride in water. For the case of volatilization (or absorption) of pesticides and other chemicals across an air-water interface, the familiar form of the two-resistance theory is

$$\frac{1}{K_1} = \frac{1}{k_1} + \frac{C_1}{H_x k_g C_g} \qquad (3)$$

where K_1 is the overall coefficient to be used with the flux equation $N_A = K_1 \, \Delta C_{A1}$ containing a liquid phase concentration difference in mol/cm^3, k_1 is the liquid side coefficient in cm/s, k_g is the gas side coefficient in cm/s, C_1 and C_g are the molar density of water and air at the existing temperature and pressure in mol/cm^3, and H_x is Henry's law constant in mole fraction form (i.e., $H_x \equiv Y_A/X_A$).

The thermodynamics of phase equilibrium of the chemical species volatilization is manifest through the Henry's law constant. Reduced to more fundamental parameters the constant

$$H_x = \gamma_A \, P_A^o / P_T \qquad (4)$$

is a term which contains the activity coefficient of molecule A in water, γ_A, the pure component vapor pressure of the chemical, P_A^o, and total pressure P_T. The activity coefficient is a physical chemistry parameter which reflects the forces of attraction or repulsion the molecule has with the surrounding layers of water molecules. Molecules which do not interact adversely with water have γ_A values of unity and those with low solubility have large positive values of γ_A. Dilling[2] developed simple formulation containing chemical vapor pressure and solubility that can be used to estimate Henry's law constant; however, the equation is limited to chemicals with finite solubility. Warner, Cohen and Ireland[3] measured Henry's law for 41 potentially toxic compounds and found that the equation obtained values corresponded closely to their experimental values. For those substances that are infinitely soluble in water, it is necessary to calculate activity coefficients directly and group contribution methods (see Sherwood, Reid and Prausnitz[4]) are most convenient to use.

Presuming concentrations in either the air or water are available, then only the appropriate gas and liquid side coefficients need be obtained to make flux calculations. In summary, Equations 1, 3 and 4 represent the and $k_g^{(n)}$ is in ft/hr (1 ft/hr = .0085 cm/s). Equation 6 results from the work of Harbeck[8]. The natural liquid-side coefficient was synthesized from stream re-aeration studies based on oxygen transfer to flowing water. The mechanical mixers impart a horizontal velocity to the surface water not unlike the velocity in natural streams. Based on detailed studies of the flow patterns in such impoundments equivalent water velocities and water depths can be chosen to use the work of Owens, Edwards and Gibbs[9]:

$$k_1^{(n)} = 1.67\ v_1^{0.67}/h^{0.85} \tag{7}$$

where v_1 is the average velocity of the surface water in cm/s, h is the depth of this moving surface layer in cm and $k_1^{(n)}$ is the oxygen absorption coefficient in ft/hr. In fairly large impoundments well away from the influence of the mechanical stirrers, it seems reasonable to use $0.035\ v_8 = v_1$ and h of one-half the impoundment water depth.

Details of transport coefficients for the turbulent zones and areas of influence will not be given here. Obviously, these parameters will be a strong function of the energy imparted to the water surface by the mechanical stirrers and the number of stirrers employed. Freeman[10] and Freeman and Klieve[11] extended the parallel resistance concept, further developed the methodology for characterizing the turbulent zone and essentially verified the model by measuring the volatilization of acrylonitrile from a laboratory simulated wastewater treatment reactor. Thibodeaux, Parker and Heck[12] recently completed extensive field measurements on methanol emissions which verify significant aspects of the model. Typical transport coefficients for this partially natural and partially machine-influenced volatilization process are shown in Table 2.

It is fairly obvious that in the above case of volatilization from wastewater treatment it is necessary to account for variations of transport mechanisms on the surface in order to obtain realistic emissions. Even this degree of adapting to circumstance will not satisfy some critics who make the case for diurnal variation in meterology, particularly the wind, as being unaccounted for, and indeed Equations 6 and 7 are only valid if wind is present. Both these equations reflect the wind speed as a parameter.

TABLE 2 NATURAL VS TURBULENT TRANSFER COEFFICIENTS FOR METHANOL IN SURFACE IMPOUNDMENTS[12]

Zone	Symbol	Average	Range (cm/hr)
gas-side, natural zone	$k_g^{(n)}$	2,680	630 to 3920
liquid-side, natural zone	$k_l^{(n)}$	9.30	2.87 to 18.0
gas-side, turbulent zone	$k_g^{(t)}$	13,900	6900 to 18,800
liquid-side, turbulent zone	$k_l^{(t)}$	8,700	2560 to 13,700

Emissions will continue under low or no-wind, conditions and chemical concentractions in air will likely be much higher in the near-field of such surface impoundments. Alternative mechanisms are operative and alternative parameterized expressions reflecting the transport circumstance need be developed and verified. Despite these criticisms, the general model is being proposed by Hwang[13] to calculate source strength when volatilization from surface impoundments is occuring in an attempt to predict downwind concentrations in air.

Vectorial Nature of Transport Coefficients

The creation of transport coefficients by definitions such as Equation 1 simplifies the flux expression but requires that the coefficient inherit all the dependence of the particular environment and circumstances of the transport. As was mentioned previously, a certain amount of vectorial flavor has also been imparted to the coefficient. This aspect is particularly important when a calibrated expressions (i.e., Equation 6 and 7) obtained under species absorption conditions is used for volatilization predictions.

Volatilization of pesticides from water surfaces involves dilute solutions both in the air and aqueous phases. The chemical flux rates are also low when compared to the rate of water evaporation from the same surface. The direction and rate of water vapor movement across the air-water interface can affect the magnitude of the K-type transfer coefficient. Bird, Steward and Lightfoot[14] present a theoretical argument of how this can occur and show the magnitude of the effect based on the film, penetration and boundary layer theories. In the case of pesticide evaporation, the movement of water vapor through the interface distorts the concentration profiles. As an example of the results of the theory, if the liquid phase controls the rate of mass transfer, the film theory rate equation is:

$$N_A = \frac{N_A}{(N_A + N_B)} k_l \ln\left\{\frac{N_A/(N_A + N_B) - x_A^*}{N_A/(N_A + N_B) - x_A}\right\} \qquad (8)$$

where N_B is water flux rate, x_A is the mole fraction of chemical A in the water and x_A^* is the mole fraction in equilibrium with that in air, Y_A. If there is a negligible amount of A in the surrounding air (i.e., $x_A^* = 0$) and $N_B >> N_A$ Equation 8 transforms to:

$$N_A = N_B\, x_A \left\{ \frac{\exp\,(N_B/k_1)}{\exp\,(N_B/k_1) - 1} \right\} \tag{9}$$

For the case of pesticides with vaporization rate controlled by the liquid phase resistance, the direction and magnitude of water vapor flux can dramatically affect the rate.

Phenomena which create interfacial turbulence can also be direction dependent. Interfacial turbulence occurs when a liquid surface moves due to interfacial tension differences created by uneven concentrations of sorbed substances on the surface. Localized density gradients near the surface due to the flux of one or more substances through the surface, can also cause interfacial turbulence. Interfacial turbulence can enhance or suppress the flux rate of chemical species moving through the interface. See Berg[15] for a review of observed interfacial turbulence effects on mass-transfer rates. The presence and/or effect of interfacial turbulence with respect to volatilization or absorption of chemicals at the natural air-water has not been reported to date to the knowledge of this author. It seems plausible that cool rain falling upon salty water, warm water, etc. would create a situation of intense density gradients at the surface and affect chemical transport rates to some degree.

The "acid rain" problem which is acute in the Northeastern United States, Canada, Sweden and other regions of the world has a dry deposition component which appears to be as important as the wet removal process. Williams[16] quantifies the net dry deposition flux with an extension of Equation 1:

$$N_A = k_c \Delta C^*_{A1} + k_d \Delta C^*_{A2} + V_g C^*_{A2} - V_r C^*_{AS} \tag{10}$$

where k_c is the turbulent transfer velocity ($\equiv D^{(t)}/\Delta y$), k_d is the molecular transfer velocity ($\equiv D/\Delta y$, D is the molecular diffusivity) V_g is gravitational settling velocity, C^*_{AS} is concentration at the water surface and V_r is the resuspension velocity. This simple formulation neglects explicit consideration of several more complex phenomena, including diffusiophoresis, thermophoresis, humidity effect on particle size and, at the interface, the roles of surface film, bubbles and sprays.

For a neutrally stratified turbulent layer over a deposition layer next to water, which will completely absorb (i.e., $V_r = 0$) the impacting molecule or particle, Equation 10 can be simplified to:

$$N_A = V_D C^*_{A,10} \tag{11}$$

where C_A^* is measured in the constant flux...(or mechanical turbulence) layer at a height of 10 meters and the deposition velocity, V_D is estimated by:

$$\frac{1}{V_D} \equiv \frac{V_{10}}{V_*^2} + \frac{1}{V_g + kV_* Sc^{-2/3}} \tag{12}$$

The first term on the right-hand side is the resistance in the turbulent layer and the second is that in the deposition layer. In this equation, V_{10} is the wind speed at 10 meters, V_* is the friction velocity, Sc is the Schmidt number ($Sc \equiv \nu/D$), and $k = 0.4$, von Karman's constant.

The vectorial nature of the deposition velocity is easily seen if one considers large particles, for which Sc is very large, being deposited under conditions where the turbulent resistance term is small. In this case, $V_D \simeq V_g$, the deposition velocity is approximated by the gravitational settling velocity of the particle. In the case of gases:

$$V_D \simeq kV_* Sc^{-2/3} \tag{13}$$

For extensions to the deposition velocity concept see Slinn and Slinn.[17]

Effect of Meteorological Conditions and Geometry on Volatilization Transport Coefficients

In order to obtain realistic volatilization rates of chemicals from specific water bodies, it will be necessary to have available the specific meteorology, micrometeorology, hydrology, water chemistry, geometry, location of man-made structures and other circumstances of the site. Coupled with this information, realistic mixing models, reaction(chemical, biochemical, photochemical) kinetics, thermodynamic, sorption, and interphase transport coefficients will be needed. This section will consist of a review of what is available with respect to transport coefficient estimation, a listing of gaps in this area which must be addressed and some numerical results that point out the variability of coefficients.

Wind and Natural Convection Driven Transport

Oxygen transport coefficients intended for purposes of water quality studies and conventionally termed "reaeration coefficients" provide a source of k_1 expressions. A report by Zison, Mills, Deimer and Chen[18] gives numerous expressions and tabulates k_1 for rivers, lakes and estuaries. The section on river reaeration is very complete. There is also a section on reaeration coefficients for stratified systems, such as stratified lakes and estuaries. Generally, the expressions contain terms for wind velocity in addition to, or in place of hydraulic parameters, since wind can be the major driving force inducing turbulence into the flow field. This is especially true in lake systems where the net advective velocity may approach zero. For stratified systems the surface transfer coefficient is only valid for a depth over which the dissolved chemical concentration can be considered constant. This depth is always less than the depth of the system. Six emperical expressions for the surface transfer coefficient of water bodies influenced by the wind are presented. The wind speed dependence appears most often in the following form

$$k_1 = a + bV^n \tag{14}$$

where V is wind speed, a, b and n are constants. Values of n reported are ½, 1, 1½ and 2 depending upon the investigator. Another functional form presented is

$$k_1 = c/(d - eV^{\frac{1}{2}}) \tag{15}$$

Wind also affects the reaeration rate of flowing water. The ultimate expression predicts the reaeration in streams with wind blowing across the surface. Apparently, wind begins to play a significant role in reaeration at speeds above 1.6 miles per hour (0.72m/s). It is possibly not sufficient to consider wind speed alone, but direction as well, in dealing with inland waterbodies protected by complex surroundings and topographic features.

A brief review of k_1 coefficients covering experimental measurements in laboratory wind tunnels and insitu measurements at the sea surface has been given by Thibodeaux.[19] Numerical values observed in wind tunnels ranged from approximately 1 cm/hr at near zero wind speed to 60 cm/hr at 30 m/s wind speed for CO_2 and oxygen. Insitu sea surface measurements ranged from 4 to 36 cm/hr for CO_2. A reported common range for O_2 at lake surfaces is given as 1.3 to 6.4 cm/hr. Of specific note in this review is the work of Cohen, Cocchio and Mackay.[20] Benzene and toluene mass-transfer coefficients of ≃ 0.5 to 2.0 cm/hr at zero wind velocity to near 40 cm/hr at 40 m/s wind velocity. A predictive expression based upon water surface roughness Reynolds number is presented.

Brtko and Kabel[21] develop models that they claim are a first attempt to actually predict liquid phase mass transfer coefficients from first principles. In particular, two models characterizing wind induced turbulence in a water body are invoked to estimate the coefficient. The "eddy cell" model result is:

$$k_1 = 0.4\ Sc^{-\frac{1}{2}} \left\{ \frac{\nu V_*^3}{kZ'} \left(\frac{\rho a}{\rho w} \right)^{3/2} \right\}^{1/4} \tag{16}$$

and the "large eddy" model result is:

$$k_1 = 1.46 \left\{ \frac{DV_*}{0.1H} \left(\frac{\rho a}{\rho w} \right)^{\frac{1}{2}} \right\}^{\frac{1}{2}} \tag{17}$$

where V_* is the friction velocity at the surface, Z′ is some depth below the surface, and H is the total depth of the water body. The other terms in the equations are k=0.4, ν, the kinematic viscosity of the water, Sc, the Schmidt number, ρa, air density, ρw, water density, D, molecular diffusivity and k_1, the liquid phase coefficient. Predicted values of both the models underestimated field measured values. The agreement for eddy cell model was best, and at the frequently observed low wind speeds, the agreement is good. The field measurements used for comparison was data gathered by R. R. Weiler from several sources and ranged from 2 cm/hr at 1 m/s wind speed to 200 cm/hr at 20 m/s. It should be noted that both these models contain a depth parameter. This work is apparently the first to include such a geometric parameter in a non-flowing, liquid phase coefficient formulation.

O'Connor, in an unpublished report by DiToro and O'Connor,[22] presents the following equation for estimating the liquid phase coefficient when the wind velocity controls the transport at the water surface:

$$k_1 = \frac{C_D^{\frac{1}{2}}}{\lambda} Sc^{2/3} \left(\frac{\rho a}{\rho w}\right)^{\frac{1}{2}} V \qquad (18)$$

where C_D is the drag coefficient and λ is "related to" the viscous sublayer fetch and height of the waves. For low wind speeds, $C_D = .0016$, $\lambda = 6$ is suggested. With $Sc = 1842$, $\rho a/\rho w = .0012$, and $V = 1$ m/s, a value of $k_1 = 0.46$ m/d (1.9 cm/hr) is reported for the volatilization of PCB from the Hudson River.

Direct evidence on chemical emissions from surface impoundments is scant. Horton, Corey and Wallace[23] present some field data on the loss of HTO from a basin 13,000 m^2 surface area and 4.5 meters in depth. Based on the tritium desorption data for a three year period, it appears that k_1 varies from 0.020 cm/hr to 0.085 cm/hr and the transport is liquid phase controlling. It also appears that the basin was likely stratified, in that the authors mention slow water mixing caused by the slight specific gravity difference between the waste containing a small amount of salt and the rainwater.

The above considerations for k_1 are limited in that they do not generally apply to those atmospheric conditions characterized by very low wind speeds or no wind. It is these conditions which are referred to as extreme meteorological conditions and that require modification of the mass transfer method. Estimation of the chemical volatilization rates in the presence of surface winds may tend to grossly overestimate the rate if an average daily rate or an average yearly rate is desired. On some days and on many nights wind ceases altogether. During this period natural convection processes would appear to control the emission rate. Sill and Gaertner[24] and Ryan and Harleman[25] consider the natural convection transport aspects of water in the gas phase above cooling ponds.

Figure 4 shows hypothetical profiles of a common natural convection volatilization situation for surface impoundments when the water (water is chemical B) is warmer than the overlying air (air is chemical A). This scenario can also occur when lakes are cooling in the fall of the year. The center profile demonstrates a decrease in water temperature as the surface is approached, equilibrium at the interface and then a further decrease in temperature with increase in distance from the interface. Both microregions (i.e., air and water) immediately adjacent to the interface are unstable thermally. The left profile demonstrates the decrease in water vapor content of the air with increase in height above the interface. The evaporating water creates an additional instability in the air microregion above the interface. The right profile demonstrates the change in concentration of the volatile chemical of interest from the water side, through the interface and then above the interface. The discontinuity at the interface is due to phase equilibrium. Due to the low concentrations on either side of the interface, it is unlikely that sizable density gradients exist due to the chemical concentration gradients there. Formally, the density gradient on the air side can be expressed by

$$\frac{d\rho_a}{dy} = \rho_a \left\{ \frac{dT}{dy}\beta + \frac{dy_B}{dy}\xi \right\} \qquad (19)$$

where $\beta \equiv \frac{1}{\rho a}\frac{\partial \rho a}{\partial T}\Big|_{Y_B P}$ and $\xi \equiv \frac{1}{\rho a}\frac{\partial \rho a}{\partial Y_B}\Big|_{T,P}$ are the coefficients of thermal expansion of the air and the coefficient of mass expansion respectively.

Correlations exist, based upon numerous experimental measurements, for heat transfer from a heated plate facing upward in a fluid. This situation simulates, to a degree, the heat transport of either side of the interface of a surface impoundment. The correlation for turbulent heat transfer is:

$$Nu = 0.14\ (GrPr)^{1/3} \qquad (20)$$

where Nu (Nusselt No.)$\equiv hL/K$, Gr (Grashoff No.)$\equiv L^3 g\beta\Delta T/\nu^2$, Pr(Prandtl No.)$\equiv C_p\rho\nu/K$, and h is the surface heat transfer coefficient, L is length of the heated surface, K is the thermal conductivity of the fluid, g is the gravi-

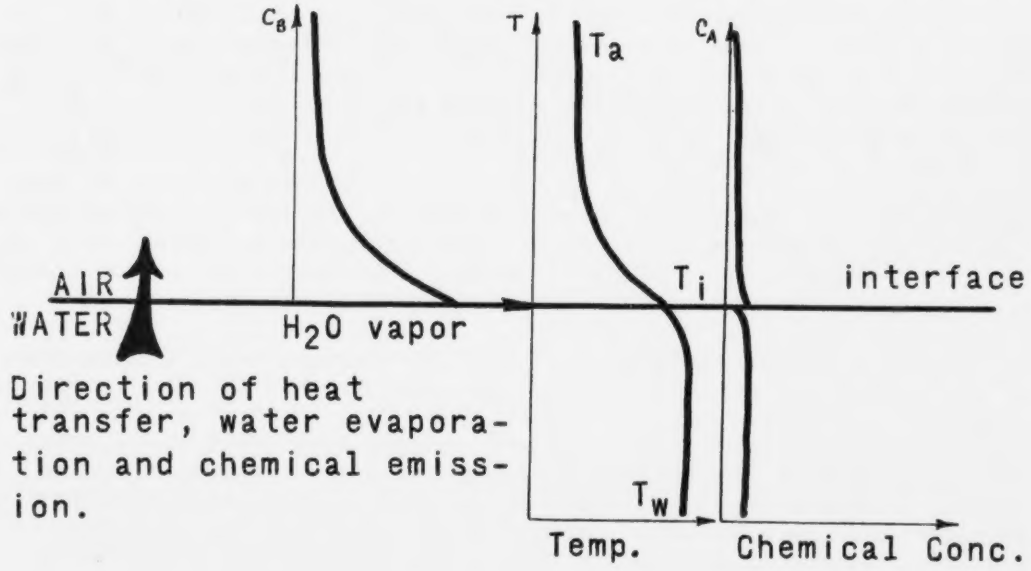

Figure 4. Natural Convection Profiles for T_w T_a.

tational constant, ΔT is the temperature difference between the interface and well beyond, ν is the kinematic viscosity of the fluid, C_p is the heat capacity of the fluid and ρ is the density. Based upon a thermal difference a heat transfer coefficient, h, can be obtained and transformed to an equivalent mass-transfer coefficient, $k_{g,T}$, by use of the Chilton-Colburn analogy:

$$k_{g,T} = \frac{hgD}{K}\left\{\frac{Sc}{Pr}\right\}^{1/3} \qquad (21)$$

An equation analogous to Equation 20 can be used to estimate $k_{g,y}$, generated by the water vapor difference:

$$Sh_B = 0.14\ (Gr_B Sc)^{1/3} \qquad (22)$$

where $Sh_B \equiv k_{g,y}L/D$, $Gr \equiv L^3 g\xi\Delta Y_B/\nu^2$.

For the purposes of demonstration, a calculation was made based on a water temperature of 31°C and air temperature of 24°C. These are typical summer temperatures for industrial lagoons. Methanol was chosen as the volatile chemical for calculation purposes. Equation 20, for each phase, yielded $hg = 3.27 J/M^2 \cdot S \cdot K$ and $h_1 = 149.36 J/M^2 \cdot S \cdot K$ and Ti (interface) = 30.8°C. Converting to the "heat transfer" generated mass-transfer coefficients yield $k_{g,T} = 811$ cm/hr and $k_{1,T} = 0.540$ cm/hr. Using Equation 22 for the gas-phase yielded a water vapor mass-transfer coefficient of 913 cm/hr. This value corrected for methanol is $k_{g,y} = 668$ cm/hr. If it is assumed that the thermal and water vapor instability derived mechanisms of transport are additive so that the sum of the coefficients can be made; then the entire gas-phase coefficient for methanol is:

$$k_g = k_{g,T} + k_{g,y} \qquad (23)$$

which yields $k_g = 1479$ cm/hr. Ryan and Harleman[22] combine the thermal and water vapor gradients by use of a virtual temperature but admit that their proposed equation is somewhat conservative at very high virtual temperatures. Deviations of 40 percent to 110 percent were displayed when compared to pond data. The two resistance equations, Equation 3, with Henry's law constant $H(\equiv y/x) = 0.27$ yields an overall liquid phase coefficient of $K_1 = 0.188$ cm/hr. Both phases contribute to the coefficient.

The above considers the case of unstable microregions near the air-water interface. For the case of neutral and stable conditions without wind, there appears to be no published material with respect to volatilization from water. In both these cases, the volatilization is controlled by molecular diffusion processes. By invoking some reasonable scenarios and simple transport models, it is possible to obtain some order-of-magnitude estimates of k_g and k_1 for the neutral and stable conditions.

The occurrence of radiation fog over low lying land or water on clear nights confirms the calmness of the winds on those nights. As the land or water radiates heat and becomes cooler, it cools the air immediately above the surface. This causes a temperature inversion to form, the temperature for some distance upward increasing with height. When the air is cooled to its dew point, fog forms. Radiation fog is often quite shallow and is usually most dense at the surface. Even on nights without fog formation extremely calm conditions do exist.

On such nights molecules of volatile chemicals desorb from the surface and diffuse upward. The molecular diffusion process becomes dominant in the evening after the convective effects of wind and thermals have subsided. It is unlikely that absolutely still air exists throughout the entire evening, but it is not unrealistic to assume that such conditions exist for a few hours. The penetration theory, which allows for unsteady state diffusion after periods of interruption, will be used as the model for chemical vaporization from the water surface and diffusing into the air layer. This process is interrupted periodically by stray air currents, the remnant of day-time currents. The penetration theory interpretation of the gas-phase coefficient is:

$$k_g = 2\sqrt{D/\pi t} \qquad (24)$$

where t is the lapse time between stray air current interruptions. Using carbon dioxide with a diffusivity in air of 0.164 cm^2/s at 25°C, yields k_g values of 27.4, 19.4, 13.7 and 11.2 cm/hr for interruption times of 1,2, 4 and 6 hours.

Another order-of-magnitude estimate can be obtained by assuming laminar air flow across the water surface and using the laminar boundary layer theory:

$$k_g = .664\,\frac{D}{L}\left(\frac{VL}{\nu}\right)^{\frac{1}{2}} Sc^{1/3} \qquad (25)$$

For a wind of 5400 cm/hr across a water surface of L = 100m in length, the gas-phase coefficient obtained for CO_2 is k_g = 12.2cm/hr. The computed values for both models are approximately 300 times less than the unstable day-time values.

Calculations similar to the above, but for the liquid phase coefficient, can be made using oxygen as a basis. The penetration theory model suggests that k_l = .287, .203, .144 and .117 cm/hr for O_2 with interruption times of 1,2,4 and 6 hours. Interruption times are the same as for air currents since the air is assumed to be the same source of disturbances for the water. Assuming the water velocity is 3.5 percent of the air velocity, a diffusivity oxygen in water of 1.80E-5 cm^2/s yield a k_l = 0.0086 cm/hr for the laminar boundary layer equation. It appears that the model predicted liquid phase coefficients can be approximately 100 times less for neutral and stable water than for unstable or day-time values.

In summary, it is instructive to display the transport coefficients in graphical form with time-of-day as the independent variable. This display is shown in Figures 5 and 6 for log k_g and log k_l of the values computed above. The diurnal variation is assumed to be dominated by calm conditions at 5:00 a.m. and windy conditions at 2:00 p.m. These times are where the minimum and maximum environmental extremes are suspected to be on a "typical" day. The variation in both coefficients is dramatic. Emission of volatiles likely decreases at night. This is also the time of day in which most odor complaints associated with surface impoundments are made. Although the rate of emission is lower, the concentration of volatile material in air is higher, due to the lack of mixing by winds or thermals.

Co-transport of Water Vapor, Geometry and Other Factors

There are several other parameters that affect chemical volatilization transport coefficients from the air-water interface to a degree that they cannot be overlooked when considering special circumstances. The co-transport of water, particularly evaporation, has been mentioned in association with Equation 9 as being one such factor. Water, due to its extremely high concentration, moves through the air-water interface at rates several thousand times faster than any other volatile component. Table 3 shows the effect that water evaporation rates can have on the liquid phase transport of pentachlorophenol. These calculations are for the film co-transport model. Similar enhancements are also predicted by the penetra-

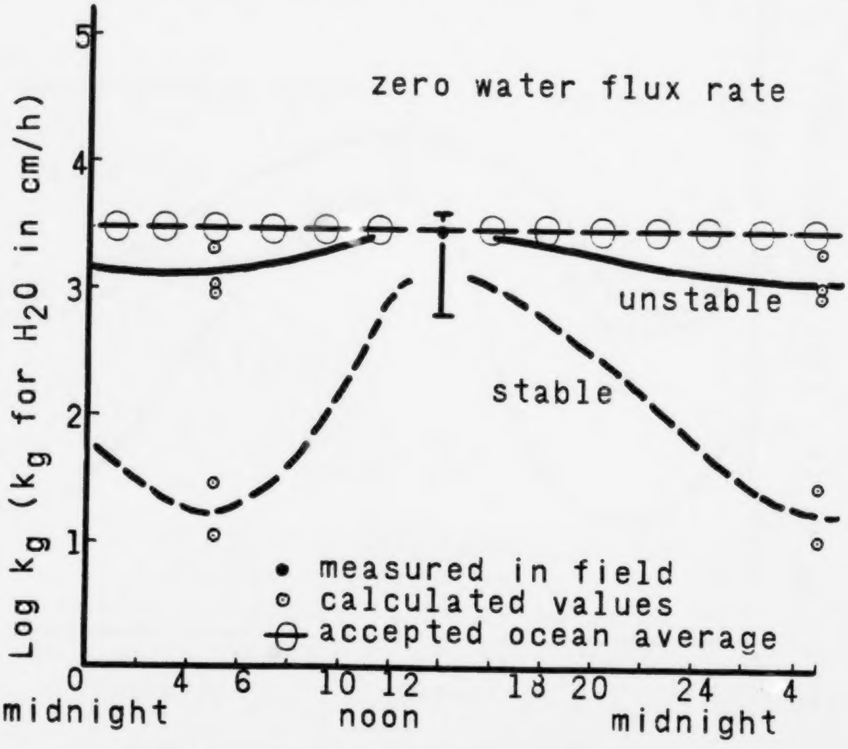

Figure 5. Diurnal Variation of Gas-Phase Coefficient.

tion and boundary layer theories.[14] Recent work by Thibodeaux, Merrill and Walbach[26] demonstrates that the flux rate of pentachlorophenol and naphthalene is tied to the evaporation rate of water during pan-evaporation "treatment" of the wastewater from the wood preserving industry. The flux equation predicted by the film co-transport model, Equation 9, and observed in the laboratory is:

$$N_A = N_B X_A \qquad (26)$$

Observed K_l for pentachlorophenol and naphthalene in laboratory pan-evaporation experiments varied from 0.18 to 1.8 cm/hr. The water evaporation rate was 0.18 to 1.35 cm/hr.

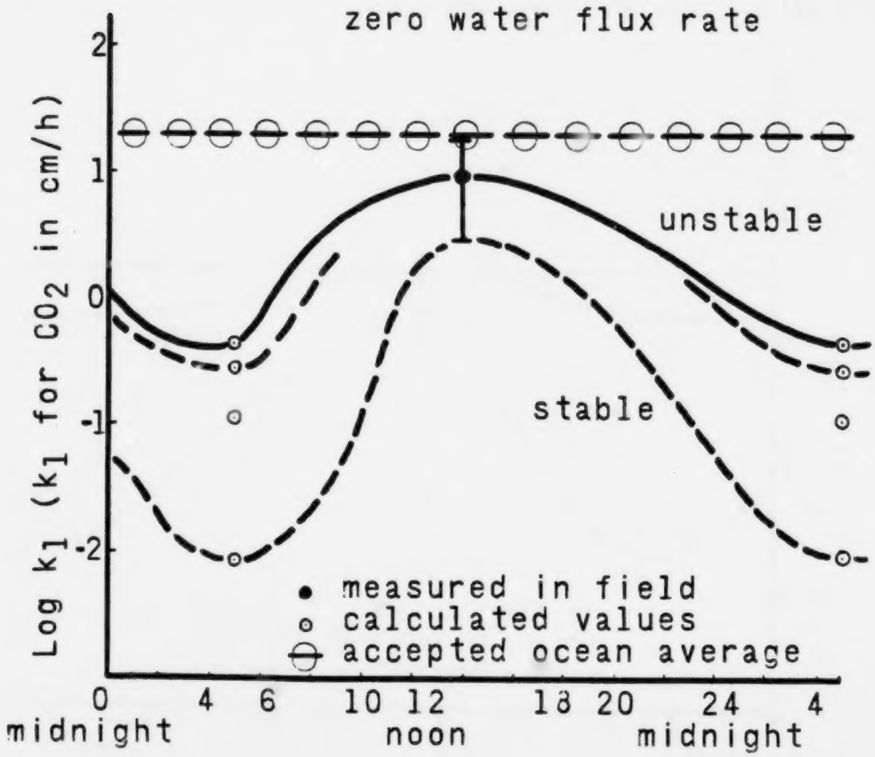

Figure 6. Diurnal Variation of Liquid Phase Coefficient.

TABLE 3 PENTACHLOROPHENOL VOLATILIZATION RATE COEFFICIENTS ENHANCED BY WATER EVAPORATION

Condition	k_1 (cm/hr)	N_B (cm/hr)	$k_1^{\bullet}$ (cm/hr)	% Enhancement
Unstable	8.12	.000	8.12	.00
	8.12	.144	8.19	.86
	8.12	.648	8.45	4.1
Stable	.187	.000	.187	.00
	.187	.144	.268	43.
	.187	.648	.669	260.

k_1 is with no water flux, $k_1^{\bullet}$ is with water flux.

Geometric factors of the surface impoundment and lake environments such as depth and fetch could have a sizable effect of k_1 values. One aspect of this is contained in the "eddy cell" and "large eddy" models of Brtko and Kabel.[21] Both models contain a water depth parameter associated with mixing and penetration of turbulence. On another scale, the resistance to air induced water movement for those basins with shallow depth need be addressed. Mixing and water currents in shallow lakes, due to wind, will likely be significantly less than those in deep lakes. The same can be questioned about the position of the thermocline on k_1 values.

Lake and ocean surface transport is affected by interactions of wind and water, which can cause high degrees of localized turbulence and transport. Measurements involving the Radon anomly and similar techniques in the near-surface waters of the ocean, yield time integrated transport coefficients that is effective for periods of weeks to a month. Phenomena such as Langmuir curculations and breaking wind-waves (i.e., whitecaps) can conceivably result in high localized volatilization. The magnitude of the effect of these and other intense events upon k_1 need be investigated before average sea-surface and lake-surface coefficients can be used with confidence.

MEASUREMENTS OF IN-SITU CHEMICAL VOLATILIZATION RATES

There are very few measurements of chemical volatilization rates from natural water surfaces. Most information and correlations have been obtained from laboratory measurements involving wind-water tanks or similar devices operated to simulate natural water surfaces. A few "field" measurements have been made in the water phase and the chemical volatilization rate inferred from disappearance rates. Current efforts associated with quantifying emissions from surface impoundments holding hazardous material may partially alleviate the lack of data. Current efforts reported by Thibodeaux, Parker, Heck and Dickerson[12] are aimed at developing air monitoring techniques which have the capability of measuring the flux of volatile chemicals from water surface. This method is an adaptation of the turbulent profile method used by pesticide chemists to measure flux of pesticides from soil surfaces. A method based upon the Gaussian plume model concept is also under development. Hopefully, the use of these two techniques will yield chemical volatilization rate data which can then be used in transport model verification studies.

SUMMARY

Although much is known concerning the volatilization of pesticides and related chemicals from water surfaces, our capability of predicting emissions must be refined to address questions of biota exposure. Emphasis is changing from the general ecosystem box-model concept to special circumstance considerations, and the exactness of the transport coefficient should change accordingly. There is a need to develop more specific transport models which necessitates study of mechanisms. The use of average transport coefficients is unrealistic. Diurnal variations in emission rates can be significant and therefore, some time dependency need be incorporated into the final algorithm. Variations due to the seasons of the year will need be incorporated also. There is a general lack of "field" data on emissions of volatile chemicals from water surfaces. This gap need be closed and laboratory derived coefficients verified with measurements of emission rates derived from air sampling methodologies or other such cross-checking means.

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MODELING HERBICIDE RESIDUE BEHAVIOR IN AQUATIC ECOSYSTEMS, USING 3,4-DICHLOROANILINE AS AN EXAMPLE*

by

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This paper presents the results of joint efforts of American and Soviet scientists under the USA-USSR Project 02.03-3I directed towards developing models of pesticide behavior in aquatic ecosystems. The proposed mathematical model incorporates the processes of pesticide volatilization from the water surface, its sorption to suspended particulate matter and bottom sediments, and chemical.photochemical and microbial degradation for a well-mixed running-water system. Using 3,4-DCA as an example, we have found dependences of the model parameters on the environmental characteristics: for the processes of volatilization - on the intensity of mass exchange in water and air, and on the Henry constant; for sorption - on the content of humic substances in suspended particulate matter and bottom sediments; for chemical degradation - on the concentration of dissolved oxygen and dissolved organic matter; for photochemical degradation - on the intensity of illumination; for microbial degradation - on the total number of microorganisms. Verification of the model performed in model ecosystems(microcosms) with waters of various composition has shown practical significance of the approach based on the use of physical-mathematical models.

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* Both sides agreed that in the Symposium proceedings this paper will be presented as an abstract only. The complete text will be published in the Soviet journal "Meteorology and Hydrology".

RATIONALE AND RESULTS OF TESTING A CHEMICAL FATE MODEL IN AN EXPERIMENTAL ECOSYSTEM

by

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Abstract

Experimental ecosystems were used to test the validity of the Exposure Analysis Modeling System (EXAMS). The experimental ecosystems were operated in the open, steady state mode and colonized with natural assemblages of organisms collected locally. Tests were carried out specifically to identify adverse effects on EXAMS' predictive capability caused by ecological complexity not incorporated in the model and by environment-specific microbial decomposition rate coefficients. No evidence was found for either adverse effect. It was concluded that EXAMS and similar models should be used with caution and that additional work is needed toward developing methodology for operating laboratory ecosystems.

PROGNOSTIC ASSESSMENT

Mathematical models are widely applied for assessment of the probable fate of toxic chemicals in the environment . One of the major specific applications in this general realm of use is prognostic analysis of new chemicals to forecast their fate prior to introduction into aquatic environments. In this application usefulness of results depends heavily upon the theoretical content of the model.

In the prognostic mode, assessment models are used in a way that requires confidence in the models' predictive fidelity over a wide range of conditions. It is not necessarily well known, a priori, what specific environments chemicals will enter. Therefore, prognostic analyses will naturally consider the fate of a new chemical in response to a wide range of environmental factors. In these analyses, combinations of factors, in general, will be found for which the chemical reaches relatively high steady state concentrations. These combinations of factors indicate potential environmental conditions under which damage could result from introduction of the chemical. For such a broad analysis the limitations of time render it infeasible to consider highly detailed representations of specific sites. Instead, low resolution descriptions of environments can be used to achieve the scope of analysis needed within a reasonable time. The level of environmental factors represented should be selected within the domain of corresponding factors in environments that are likely to receive the chemical, but it is not necessary that any real environment correspond to any of the particular hypothetical ones selected for prognostic analysis.

In analyses of this sort, the kind of information sought is an expected behavior pattern for the fate of the chemical. In form this kind of information is much like a summary that one could make if he were knowledgeable of the behavior of a real chemical that had been widely used for many years. Of course prognostic analysis summaries are necessarily of lower confidence than are summaries of observed behavior. They provide a potential, however, for regulation of harmful chemicals without the necessity of first experiencing the environmental damage. This information will probably prove most useful in planning for specific data requirements prior to complete formulation of regulatory rules for the chemical. For such information to be useful, a high level of confidence must exist that the results are generally correct. Many factors conspire to make it unlikely for this confidence to be derived from cumulative experience. Among these is the use of prognostic analyses alone for new chemicals, the long lag time between use of a chemical and the acquisition of useful data, and the probable predominance of hypothetical environments, or at least low resolution representations of real environments, in prognostic analyses.

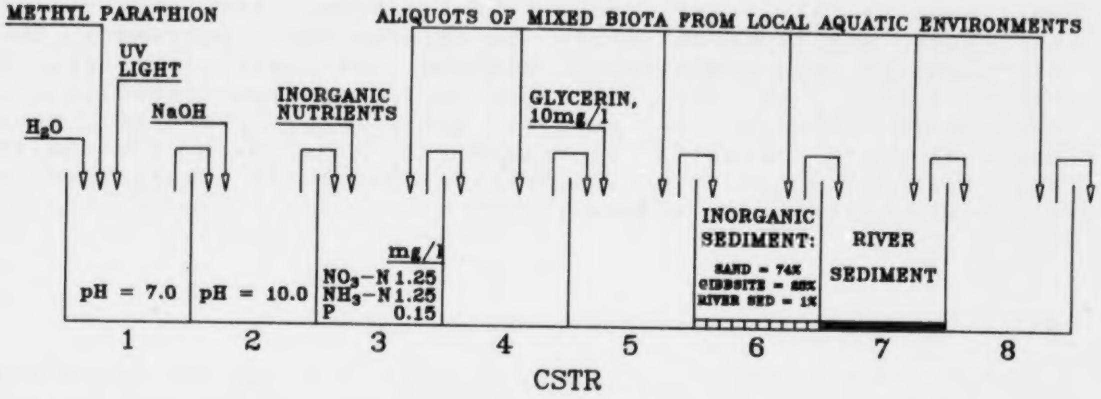
Confidence in the results arises primarily from two bases. The first basis derives from the consideration that models used in prognostic analyses (e.g. the Exposure Analysis Modeling System, EXAMS) are comprised of expressions based upon the current state of understanding of the chemistry and biology of xenobiotic organic chemicals. Aspects of chemical behavior that are influenced by these model components, therefore,are based upon the current state of science. Representations of transport processes and temporally varying environmental factors are purposefully simplified to permit rapid analyses that are broad in scope with respect to environment. If the selected level of resolution for prognostic analyses is accepted, EXAMS represents the best capability possible at the current state of science. Still, one would prefer to have some empirical confirmation, as well as some quantification of a model's predictive capabilities. The second basis provides some of this empirical confirmation. It is useful to consider the nature of the confidence that is needed for results with a new chemical and a hypothetical environment. Assurance is needed that, for such environments that exist, results of the model and observations on those environments would be in acceptable agreement This statement of need essentially defines the characteristics of tests that, on the one hand, could increase credibility of prognostic results, or on the other hand, uncover model deficiencies. Results of tests in this vein provide the empirical basis for the appropriate level of confidence in prognostic assessment models.

BASIS FOR TESTS OF ASSESSMENT MODELS

Laboratory ecosystems are simple systems that can be described, for our purposes, at the level of resolution of the hypothetical environments of prognostic assessments. As such they constitute an instance of environments with which we expect EXAMS' predictions to be in acceptable agreement. Laboratory ecosystems are not subject to the vagaries of weather. This removes the possibility that variation due to uncontrolled weather influences will either render tests uninterpretable or lead to a spurious interpretation. Because of these properties, laboratory ecosystems were selected as test systems.

The laboratory ecosystems used for these tests were located at the EPA's Environmental Research Laboratory, Athens, Georgia. Eight systems were maintained with different levels of environmental factors (Figure 1). These systems were well stirred, the environmental factors were maintained at constant levels (except for light levels to simulate day and night), and the mixed biological communities were allowed several weeks to stabilize before the experiments began. In this mode of operation the laboratory ecosystems were considered to be well suited to representation in the same manner as the hypothetical environments of the prognostic analyses. We used the EXAMS to make predictions of expected concentrations in these ecosystems and compared these predictions to measured results to test whether, in these instances, model results and observations were in acceptable agreement.

As noted above, in such a test, if model results are in acceptable agreement with observations, then credibility is increased. As Polya (1954) expressed it, the model has become "more plausible." A test of a model is most profitable, however, if it identifies existing deficiencies. If the model results are found not to be acceptably close, the problem exists of identifying the cause of the discrepancy. In anticipation of this problem we designed our experiments specifically to test for two potential problems. EXAMS and other models for the fate of chemicals in the environment have been criticized as being subject to these two problems. First is the general criticism that the model, in calculating the disappearance of a compound


METHYL PARATHION
ALIQUOTS OF MIXED BIOTA FROM LOCAL AQUATIC ENVIRONMENTS
UV LIGHT
H_2O
NaOH
INORGANIC NUTRIENTS
GLYCERIN, 10mg/l
pH = 7.0
pH = 10.0
mg/l
NO_3-N 1.25
NH_3-N 1.25
P 0.15
INORGANIC SEDIMENT:
SAND = 74%
GIBBSITE = 25%
RIVER SED = 1%
RIVER SEDIMENT
1
2
3
4
5
6
7
8
CSTR

Conditions

H_2O Flow = 500 l/Day
CSTR Retention Time = 12 Hr
Mixing Rate = 2 RPM
H_2O Temp = 20°C
Light = 2500 or 3000 Foot Candles
(12 hr light, 12 hr dark)

Figure 1 Schematic of the conditions imposed on the series of CSTRs to maintain different environments

by joint operation of several processes whose rates can be determined separately in the laboratory, ignores complex ecosystem processes such as symbioses. It is considered that these complexities might render chemical behavior unpredictable by such models. Second is the criticism that the process of biological decomposition cannot be adequately described by a second order or other description in which the rate is proportional to measured microbial density. It is often asserted that biological decomposition is a more complex and as yet unknown function of environmental factors.

If ecological complexities cause chemical fate to deviate from that predicted by EXAMS, then the more complex the system, the higher the probability that such deviation will occur. To provide the greatest opportunity for such potential complexities to be expressed, we developed duplicates of six different open aquatic systems (two of the total of eight environments were essentially abiotic). These ecosystems were developed in separate, serially connected, 240-liter compartments housed in a controlled environment chamber (Holm et al., 1981). The average residence time in each compartment was 12 hours. The environments differed primarily in their chemical inputs and their position in the serially connected, flow-through series. Corresponding to these differences, different biological communities developed in each environment. To promote high diversity we obtained samples of organisms from several local environments and introduced them weekly into each of the environments. During this time the test chemical, methyl parathion (MP), was introduced into the upstream environment in both of the duplicate series. After approximately 6 weeks, measured system values were acceptably stable. We then measured MP concentration and the parameters used to specify hypothetical environments on each of the environments. These measurements were taken four times at intervals of two weeks, with the exception of the last sample which was separated from the third sample by one month.. With this mode of operation of the laboratory ecosystems, a high degree of complexity developed in the microbial, algal, and small metazoan groups of organisms (Holm et al., 1981). The systems are not large enough to permit development of stable, complex vertebrate or even macroinvertebrate subcommunities. We expect the fate of a toxic chemical to be predominantly influenced, however, by the microbial and algal subcommunities. These laboratory ecosystems, therefore, provided the conditions for expression of synergistic and other ecological effects if they exist.

The concern that biological decomposition rate may not be described as a process in which rate is proportional to microbial density needs elaboration. The concept that underlies this concern is the widely held view that microbial decomposition of specific xenobiotic compounds is carried out by specific microbial populations. There is no prior reason to suspect these specific populations, dependent as they presumably are upon particular classes of compounds, to be in constant proportion to the measurable microbial densities for different environments. On the other hand, in a study of microbial decomposition of three chemicals in over 40 water bodies, very little variation (coefficient of variation of about 65%) was found in second order decomposition rates (Paris et al., 1981)

The possibility that microbial decomposition is a process that can be described by a model that is first order with respect to chemical concentration only, often has been suggested. This possibility can be rejected on both logical and practical bases for use in prognostic assessments, even where a limited data set seems to bear it out. The logical basis for its rejection is simply the following. If organisms carry out the decomposition, then, clearly, the process is appropriately described only by expressions that are some function of the quantity of organisms. The first order description is independent of quantity of microorganisms, and, therefore, it is inappropriate.

Assuming that the disappearance rate is proportional to the chemical concentration one could use a first order term to represent each environment and each condition. This approach would beg the question, however, of what is the appropriate descriptor. More importantly, it would make prognostic assessments practically impossible by requiring environment-specific first order rate coefficients for each chemical and each environment.

An appropriate descriptor for microbial decomposition must be a function of microbial population density and concentration of the chemical. The simplest meaningful function that includes both variables is the second order expression:

$$k[B][S]$$

where k is the second order rate coefficient, [B] is the concentration of biomass, and [S] is the concentration of the chemical. One other commonly used expression, the Monod or Michaelis-Menten expression, reduces to the second order expression when substrate concentration is very low relative to the half saturation constant. The expression for second order kinetics is a good initial choice, therefore, for describing microbial decomposition (Paris et al., 1981). Use of this expression is based upon the underlying assumption that the second order rate coefficient is a property of the chemical; that is, it is independent of the environment. The degree to which this assumption holds true is an open question.

The question is critically important for prognostic assessment. At issue is whether analyses for various environmental conditions are of benefit without specific microbial first order rate coefficients for those conditions. If second order microbial decomposition rate coefficients are not a function of environment, then assessments can proceed based upon one set of information on the chemical, a set of descriptive information for each environment, and no environment-specific information about the chemical.

We tested this question by making predictions in two ways. One set of predictions employed second order, biological decomposition, rate coefficients specific to the environment and time of prediction. These coefficients were estimated in independent experiments on the specific environments within two days of the time for which the prediction was made. For the other set of predictions, a single, overall, average biological decomposition rate coefficient was used for all predictions. Microbial densities used in both kinds of predictions were measured separately in each environment. If biological decomposition is a function of specific populations that vary from environment to environment, we expect improved predictions. That is, predictions made using rate coefficients from specific environments should be a significant improvement over those made using a single, average rate coefficient for all environments.

RESULTS

If predictions and observations are identical, a regression analysis of observed versus predicted concentrations will result in a linear relationship with unit slope and zero intercept Accordingly, we carried out regression analyses for both sets of predictions. Our null hypotheses were

H_0: intercept = 0

H_0: slope = 1

and alternate hypotheses were

H_a: intercept = 0

H_a: slope = 1

We were unable to formulate an objective criterion to establish the probability level for rejection of the null hypothesis. Instead, we decided to use the tests as guides for further consideration of the model. That is, whenever test results gave rise to reasonable doubt about the model's validity, we sought the cause in both model and experiment.

The hypotheses were the same using both specific biological decomposition rate coefficients and averaged ones. All data gathered during the experiment are graphed as a function of specific environment in Figure 2. Table 1 contains summarized results of the tests for specific rate coefficients, and Table 2 for averaged ones. The test statistic is Student's t, and "P>t" is the probabilty of a greater value of t by chance alone. A graph of predicted concentrations of MP using specific rate coefficients versus observed concentrations is presented in Figure 3.

During the interval (approximately one month) between the third and fourth sampling, marked visible changes occurred throughout the systems. These changes were accompanied by variations in the system parameters such as greater amplitudes of fluctuations in pH and dissolved oxygen (Holm et al., Appendices 21-28). Because of these phenomena, we chose to carry out an additional set of analyses in which date 4 was analyzed separately from the other dates. Data for specific biological decomposition rate coefficients were available only for dates 3 and 4.

With dates 3 and 4 combined there is no evidence that predicted concentration differs from the observed concentration when environment-specific rates are used. With averaged rate coefficients and with date 4 combined with all other dates, however, both intercept and slope differ significantly from the hypothetical values, providing evidence that predicted

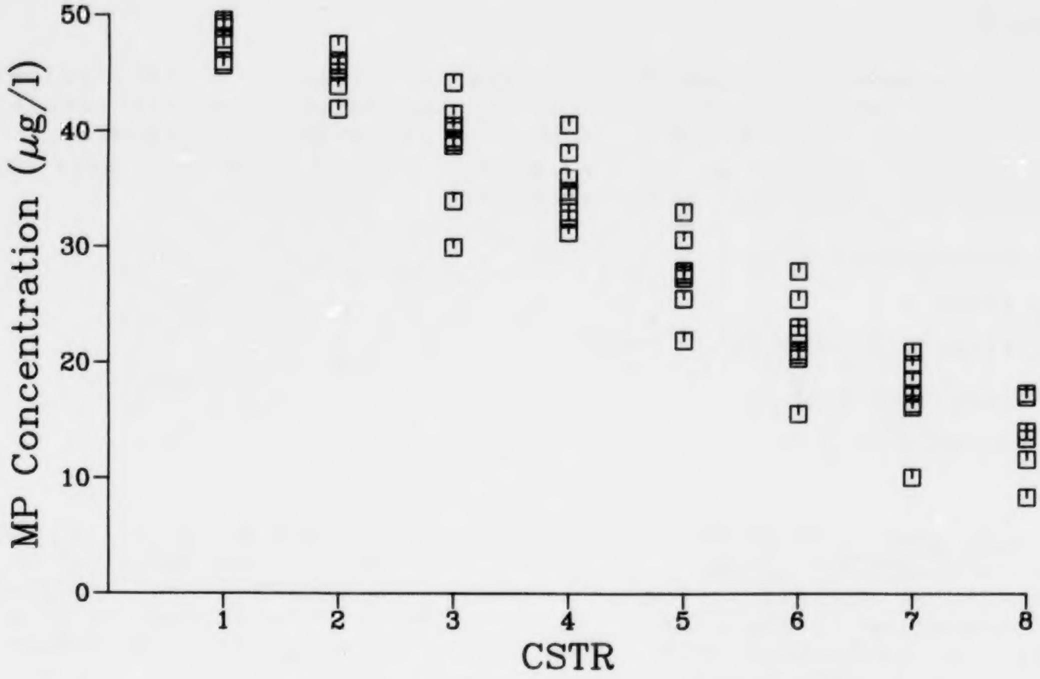


Figure 2. Graph of methyl parathion concentration plotted as a function of specific experimental environment (CSTR)

concentrations differ markedly from the observed concentrations. When date 4 is considered separately, however, the results are rather different. There is evidence, although perhaps weak, for differences between predicted and observed for date 3 using environment-specific rate coefficients, but no evidence for differences at date 4 (Table 3). With the averaged rate coefficient, no differences are evident for dates 1-3, whereas

Table 1. Tests of intercept = 0 and slope = 1 from regression of observed on predicted concentrations for environment specific biological decomposition rate coefficients

dates 3 and 4 n=20 r^2=.87		parameter value	t	P > t
	intercept	2.75	1.18	.25
	slope	.91	1.10	.29

Table 2. Tests of intercept = 0 and slope = 1 from regression of observed on predicted concentrations for averaged biological decomposition rate coefficients

dates 1 - 4 n=71 r^2=.71	parameter value	t	P > t
intercept	7.10	3.40	<.01
slope	.83	2.67	.01

with date 4 differences clearly exist between predicted and observed concentrations.

The changes in the systems between sampling dates 3 and 4 occurred only in the environments with biota. One additional regression analysis was carried out incorporating only

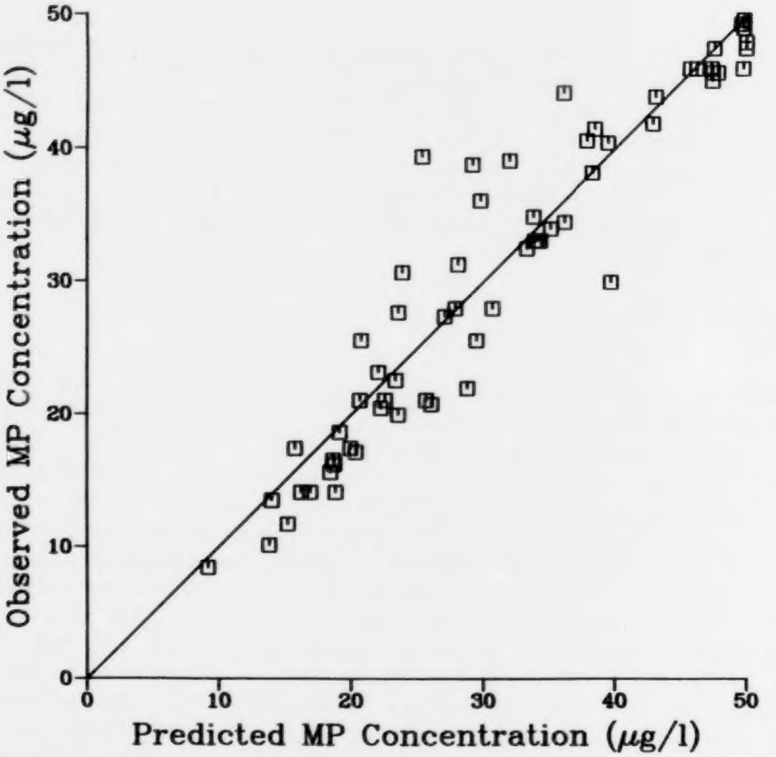


Figure 3. Graph of observed versus predicted methyl parathion concentrations. Predictions were made using EXAMS

Table 3. Tests of intercept = 0 and slope = 1 from regression of observed on predicted concentrations for environment specific biological decomposition rate coefficients; sampling date 4 analyzed separately.

		parameter value	t	P > t
date 3 n=12 r^2=.93				
	intercept	4.54	2.41	.04
	slope	.82	-2.63	.03
date 4 n=8 r^2=.82				
	intercept	-2.93	-.45	.67
	slope	1.13	.60	.57

environments with biota for averaged biological decomposition rate coefficients on date 4 (Table 5). For this analysis the mean square error was high (about 45) and the coefficient of determination was only 0.46. Against this variation the intercept estimate, 8.02, was not judged significantly different from zero and the slope is very close to one Hence, again there is no evidence for differences between predicted and observed values.

DISCUSSION

The experiments were carried out to test the existence of complex ecosystem effects leading to low predictability, and to test for environmental specificity of the biological decomposition rate coefficient. In regard to the latter, there is little evidence for environmental specificity of the rate coefficient. When all dates were analyzed together there appeared to be such evidence. When decomposed to allow for known disturbances, however, the evidence was mixed. On date 3 (Table 3) there appears to be evidence directly against environment-specific rate coefficients at least as we measured them. And on date 4 (Table 4) there is evidence against the use of a single value for the rate coefficient. When the abiotic environments were discounted, however, even this bit of evidence disappeared. It is known that factors of the environment, other than those that can be considered reactants (such as the hydrogen ion or bacteria) affect the second order rate. For example, temperature certainly affects the rate signficantly if a broad enough temperature range is considered. Temperature, however, is included in EXAMS, whereas most other properties of the environment are not. Our tests must be considered to be tests of whether these complex properties of the environment, which we excluded from the model, affect its predictive capability by affecting the second order rate coefficient. We concluded that, over the range of factors that existed in our systems, any such effects must be small.

Generally, the tests suffer from small sample sizes and high variability. It might be argued that this is evidence of complex ecosystem phenomena reducing predictability. It is more probable, however, that the variability resulted from imperfect operation of laboratory ecosystems. Few studies have been made toward developing a technology of experimental ecosystem operation, even though a great deal of experience exists for various types of microcosms. Laboratory ecosystems, however, should be clearly distinguished from microcosms, or at least viewed as a special case. Microcosms typically have been operated as closed systems and have seldom been operated with highly diverse naturally derived biota (Brockway et al., 1978; Lassiter, 1978). A property usually associated with natural ecosystems is that their characteristic biotic components are derived from highly diverse biota from outside the system through competition for resources. The competition within a given ecosystem is unique to that system as a result of unique abiotic factors. When these charaacteristics are preserved,

Table 4. Tests of intercept = 0 and slope = 1 from regression of observed on predicted concentrations for averaged biological decomposition rate coefficients, dates 1 - 3 analyzed separately

		parameter value	t	P > t
dates 1 - 3 n=48 r^2=.87				
	intercept	- .31	- .16	.87
	slope	.99	- .23	.82
date 4 n=23 r^2=.66				
	intercept	17.64	5.64	<.01
	slope	.64	-3.57	<.01

Table 5. Tests of intercept = 0 and slope = 1 from regression of observed on predicted concentrations for averaged biological decomposition rate coefficient; sampling date 4 omitting environments 1 and 2.

date 4 n=17 r^2=.46	parameter	value	t	P > t
	intercept	8.02	1.40	.18
	slope	1.12	.43	.67

laboratory systems can be referred to legitimately as ecosystems. In this view microcosms that are operated as described (closed systems, artificially chosen biota, etc.) are not ecosystems. Our approach, however, was to preserve the biotic diversity and derivation of climax communities through competition under characteristic environmental conditions. Therefore, we refer to our systems as laboratory or experimental ecosystems.

In most scientific disciplines there are characteristic laboratory apparatus, such as the particle accelerator of particle physicists. Use of the apparatus is beneficial in a given experiment because it provides appropriate conditions, and because its operating characteristics are well known relative to the scientific question being studied. The laboratory ecosystem can be considered an apparatus for ecological or environmental science studies. The major drawback deterring use to its full potential, however, is the low level of experience with its routine operation. Because we are developing this experience base concurrently with the model tests, we expect some degree of unexplained variation in the data from early experiments, but improvements thereafter. Laboratory ecosystems are of high potential for ecosystem and environmental science studies, but much is yet to be learned in regard to their consistent operation.

Overall, no evidence was produced in these studies to indicate that the biological decomposition rate coefficient is environment-specific. Likewise, no evidence arose implicating synergisms or other complex ecosystem phenomena, other than high variability. The lack of evidence for these specific, potential problems favors continued, cautious application of models for prognostic assessments. It was concluded that more work was needed toward developing the experience base for operating laboratory ecosystems.

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This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

VERIFICATION OF A TOXICS FATE AND TRANSPORT MODEL

by

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ABSTRACT

A mathematical model of the fate and transport of pesticides (or other toxics) has been developed and applied to two reservoirs in Iowa. The insecticide dieldrin and the herbicide alachlor were simulated. Soluble and biodegradable herbicides were shown to have considerably different fate than chlorinated hydrocarbon insecticides. Utility of the model was demonstrated under steady flow and unsteady state conditions. Bioconcentration was included to assess biological effects of dissolved toxic chemicals.

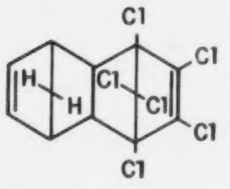
INTRODUCTION

Agricultural usage of pesticides in Iowa is widespread, particularly grass and broadleaf herbicides and row crop soil insecticides. One of the insecticides widely used for control of the corn rootworm and cutworm from 1960 to 1975 was the chlorinated hydrocarbon, aldrin. Aldrin is microbially metabolized to its very persistent epoxide, dieldrin. Dieldrin is itself an insecticide of certain toxicity and is also a very hydrophobic substance of limited solubility in water (0.25 ppm) and low vapor pressure (2.7×10^{-6} mm Hg @ 25°C). It is known to bioaccumulate to levels as high as 1.6 mg/kg wet weight in edible tissue of Iowa catfish [1].

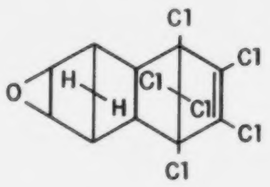
Aldrin application in Iowa during the mid-1960's amounted to some 2.94×10^6 kg/yr on 5.0 million acres (2×10^{10} m^2). However, the corn rootworm grew increasingly resistant to aldrin and after 1967, usage decreased across the state by approximately one-half. Finally, the pesticide was banned in 1975 and very little was applied after 1976. Although aldrin was no longer labeled, dieldrin residues in excess of the Food and Drug Administration "action" level (0.3 mg/kg wet edible tissue) were recorded for Coralville Reservoir fishes, and commercial fishing was banned in 1975. The problem is to determine the fate and transport of the pesticide dieldrin and to assess when the residual concentrations will be acceptable for commercial fishing.

One of the most widely used herbicides in the U.S. and Iowa is the soluble, acetanilide alachlor (Lasso^R). It is applied at 1.1 kg/ha as a preemergent for grass control in corn during the period from mid-April to mid-May (see Table 1 for structure). Concentration in Iowa waters range 1-100 μg/ℓ in headwater streams with dilution and biodegradation accounting for lower concentrations (∿1 μg/ℓ) in large rivers directly after application. The fate of alachlor (Lasso) is simulated for a large reservoir in south-central Iowa, Lake Rathbun.

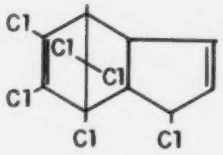
Coralville Reservoir is a mainstream impoundment of the Iowa River in Eastern Iowa. It drains approximately 7978 km^2 of prime Iowa farmland and receives extensive agricultural runoff with 90% of its drainage basin in



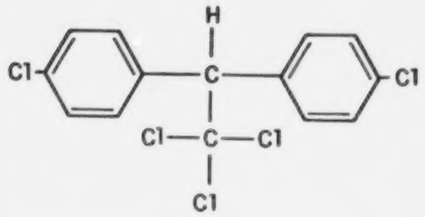
ALDRIN



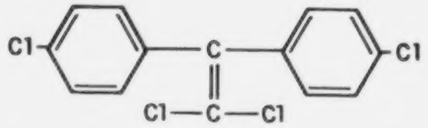
DIELDRIN



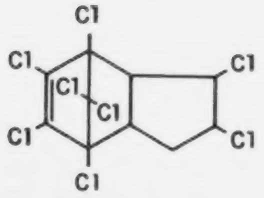
HEPTACHLOR



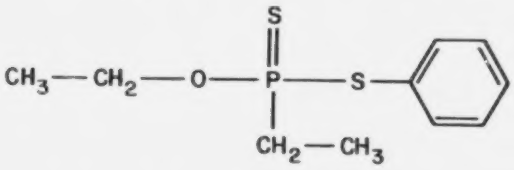
DDT



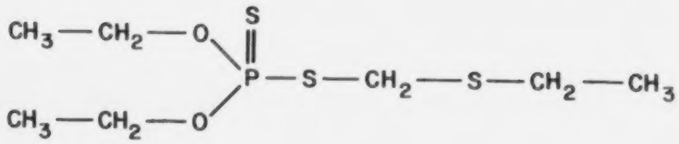
DDE



CHLORDANE

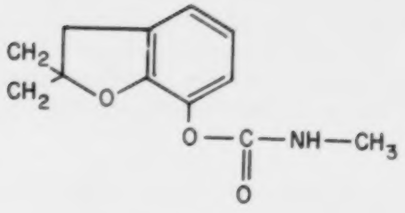


FONFOS

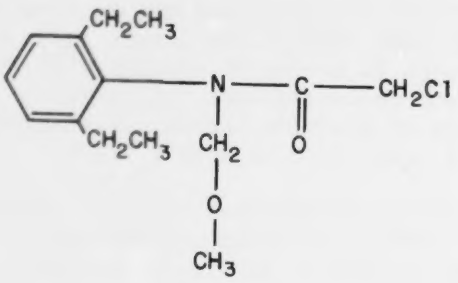


PHORATE

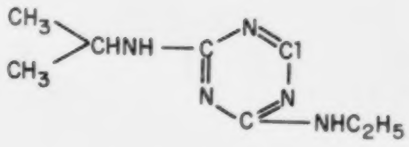
Table 1. Chemical Structures of Selected Iowa Pesticides



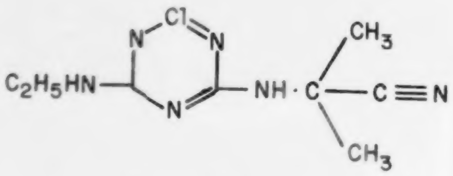
CARBOFURAN



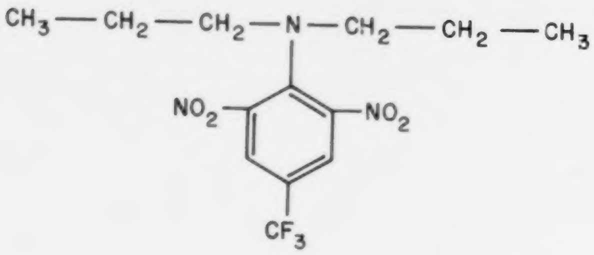
ALACHLOR



ATRAZINE



CYNAZINE



TRIFLURALIN

Table 1. (Cont.)

intensive agriculture. It is a variable-level, flood control and recreational reservoir which has undergone considerable sedimentation since it was created in 1958. At conservation pool (680 ft. above msl), the Reservoir has a capacity of 4.69 x 10^7 m^3, a surface area of 1.98 x 10^7 m^2, a mean depth of approximately 2.44 m, and a mean detention time of 14 days. In 1958, the capacity at conservation pool was 6.63 x 10^7 m^3.

Several models have been developed to assess the fate and transport of agricultural chemicals including the Agricultural Runoff Model (ARM) [2], the Nonpoint Source Pollution Model (NPS) [3], the Stanford Research Institute Kinetic Model (SRI) [4], and the Exposure Analysis Modeling System (EXAMS) [5]. The first two models are primarily designed to simulate the delivery of soil particles and agricultural chemicals to the edge of the stream bank. They make extensive use of the modified Universal Soil Loss Equation and knowledge of the chemical partitioning between soil and water, together with a given flood hydrograph. The SRI and EXAMS models are kinetic formulations which describe the chemical, physical and biological reactions which a pesticide can undergo once it reaches the water body. Chemical hydrolysis, volatilization, photolysis, and biological degradation comprise the reactions considered in these models. Instantaneous adsorption and desorption equilibrium is also assumed. Relative importance of the pathways of pesticide fate (hydrolysis, volatilization, photolysis, biological degradation, oxidation, and sorption) may be assessed in the laboratory [4].

Previous models have not been extensively verified with field data, and they have not combined fate and transport modeling with the biological effects (bioconcentration). In this paper, a pesticide transport and bioconcentration model is developed and applied to Coralville Reservoir to assess the fate and effects of dieldrin in the ecosystem. Results have aided the Iowa Conservation Commission in their decision to lift the commercial fishing ban on November 7, 1979.

MODEL DEVELOPMENT

A schematic of pesticide fate and transport within a reservoir is presented in Figure 1. The solid lines are in accordance with the SRI model formulation [4]. Modifications in both the kinetics and transport (which might add increased realism to the model) are represented by dashed lines. A two-compartment or "pond" representation of the reservoir was assumed since there exists little in-reservoir data for which to calibrate a multi-compartment model. Figure 2 gives the physical configurations of the completely mixed compartments utilized in the model. Coralville Reservoir dimensions were used in the pond configuration for model calibration, and simulations were later performed using the lake configuration as well.

Although the field data reflects individual storm events, the goal here was to represent annual average concentrations and mass flows. Therefore, constant annual average inflow and outflow rates were assumed, together with an average annual volume for the reservoir. Coralville Reservoir does not thermally stratify to any great extent, so the failure to include a hypolimnion compartment in the pond configuration is not viewed as a serious problem.

In addition to chemical reaction pathways, fish uptake and depuration (excretion and metabolism) was included in the model. The bioconcentration part of the model formulation is depicted separately in Figure 3. Biouptake is proportional to the product of the fish biomass and the dissolved pesticide concentration. Pesticide is removed by the fish as water passes the gill membrane. Biouptake from sediment and/or food (prey) items could also be included in this portion of the model. Here it is assumed that the pesticide residue is metabolized within the fish, but in some cases it may be necessary to recycle the depurated pesticide as a dissolved input.

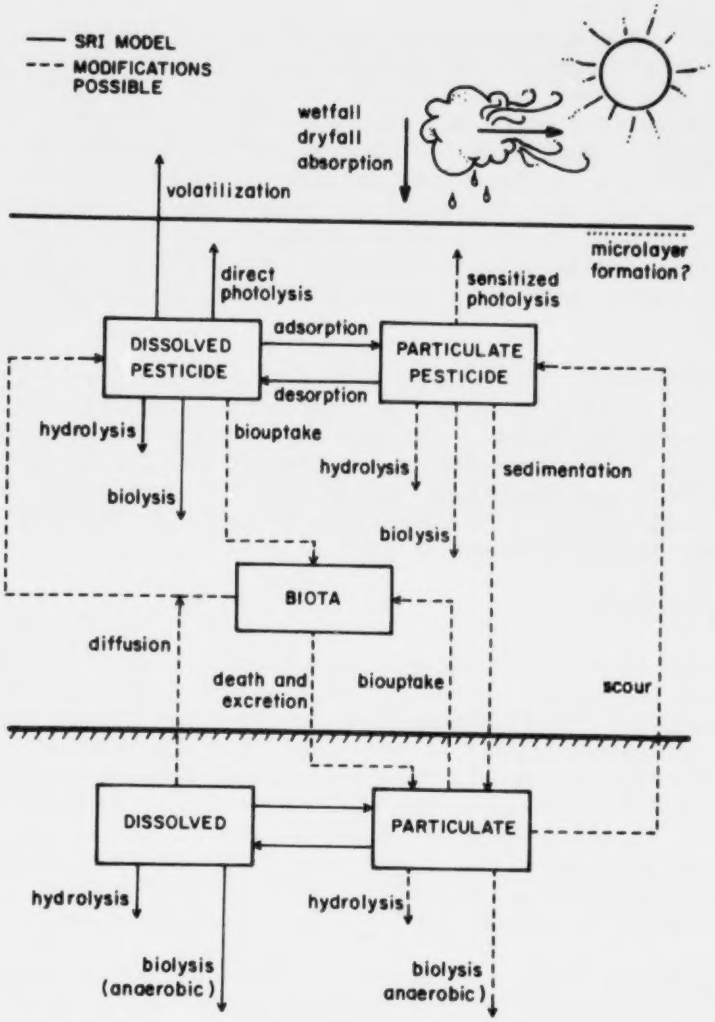

SRI MODEL
MODIFICATIONS POSSIBLE
wetfall
dryfall
absorption
volatilization
direct photolysis
sensitized photolysis
microlayer formation?
adsorption
DISSOLVED PESTICIDE
PARTICULATE PESTICIDE
desorption
hydrolysis
biouptake
biolysis
hydrolysis
sedimentation
biolysis
BIOTA
diffusion
death and excretion
biouptake
scour
DISSOLVED
PARTICULATE
hydrolysis
hydrolysis
biolysis (anaerobic)
biolysis anaerobic)

Figure 1. Pesticide Fate and Transport

Mass Balance for Pesticides in Reservoirs

The distribution of pesticides in reservoirs is established by application of the principle of continuity or mass balance. Each phase, the dissolved and particulate, is analyzed separately, taking into account the interaction with the other. Thus for the dissolved component, the mass balance includes various reaction pathways [4] in addition to the inflow and outflow. The basic differential equation can be written to include the sum of the first order or pseudo-first order reactions (hydrolysis, biological degradation, biological uptake, photolysis, and volatilization) as well as adsorption and desorption kinetics as a function of particle size distribution:

$$\frac{dC}{dt} = \frac{W_c}{V} - \frac{C}{t_o} - \sum_{i=1}^{4} k_i C - \sum_{j=1}^{n} k_{f_j} M_j C + \sum_{j=1}^{n} k_{r_j} C_{p_j} \quad (1)$$

in which

V = reservoir volume L^3

W_c = rate of mass input of the dissolved component, M/T

t_o = mean hydraulic detention time

C = dissolved chemical concentration

$\sum_{i=1}^{4} k_i$ = sum of the first order decay rate constants including the following:

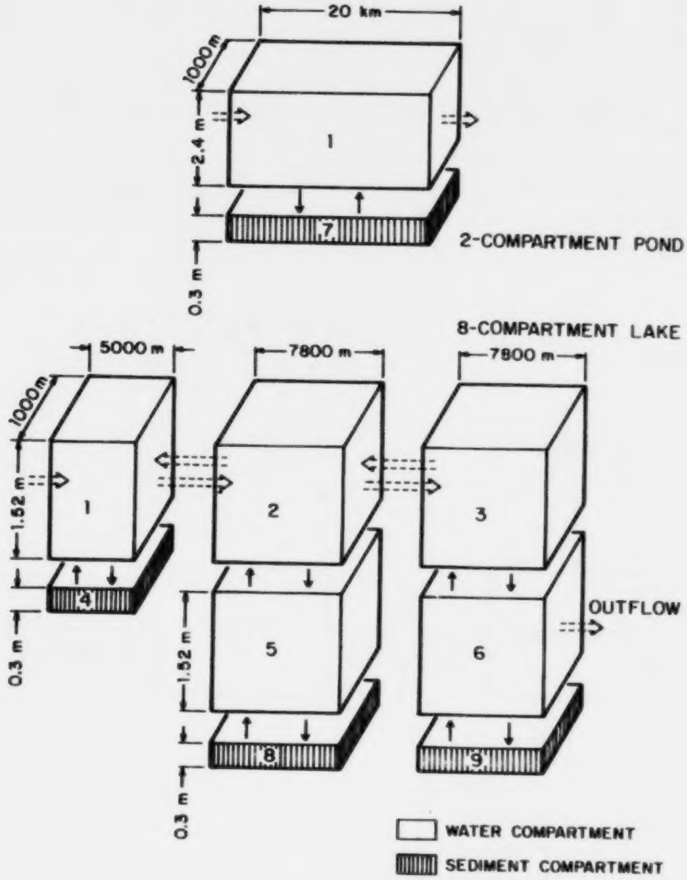

20 km
1000m
2.4 m
1
7
0.3 m
2-COMPARTMENT POND
8-COMPARTMENT LAKE
5000 m
7800 m
7800 m
1000m
1.52 m
1
2
3
4
0.3 m
1.52 m
5
6
OUTFLOW
8
9
0.3 m
WATER COMPARTMENT
SEDIMENT COMPARTMENT

Figure 2. Physical Configurations of the Reservoir Model

$k_1 = k_2'$ [Bacteria] = pseudo-first order biological degradation rate constant, T^{-1}

$k_2 = k_2'$ $[OH^-]$ = base catalyzed, pseudo-first order hydrolysis rate constant, T^{-1}

$k_3 = k_3'$ (quantum yield) = first order direct photolysis rate constant, T^{-1}

k_4 = first order volatilization rate constant, T^{-1}

$\sum_{j=1}^{n} k_{f_j}$ = sum of the adsorption rate constants for the j^{th} size fraction, n total fractions, $L^3/M\text{-}T$

M_j = suspended solids concentration in the j^{th} size fraction, M/L^3

$\sum_{j=1}^{n} k_{r_j}$ = sum of the desorption rate constants for the jth size fraction, n total fractions, T^{-1}

C_{p_j} = particulate chemical concentration due to the jth size fraction, M/L^3

If we do not partition the suspended solids concentration into various size fractions or if only one size fraction is active in sorbing the chemical of interest, then Equation 1 reduces to:

$$\frac{dC}{dt} = \frac{W_c}{V} - \frac{C}{t_o} - \Sigma kC - k_f MC + k_r C_p \qquad (2)$$

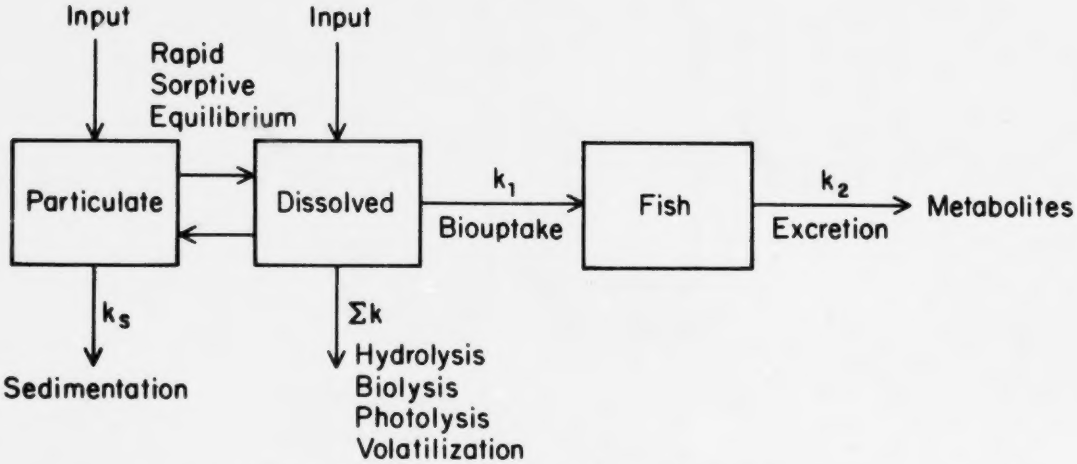

Input
Input
Rapid
Sorptive
Equilibrium
Particulate
Dissolved
k_1
Biouptake
Fish
k_2
Excretion
Metabolites
k_s
Sedimentation
Σk
Hydrolysis
Biolysis
Photolysis
Volatilization

Figure 3. Bioaccumulation Kinetics of the Pesticide Transport Model

in which

Σk = overall decay coefficient of the dissolved chemical, T^{-1}

For the particulate chemical concentration in the j^{th} size fraction:

$$\frac{dC_{p_j}}{dt} = \frac{W_{p_j}}{V} - \frac{C_{p_j}}{t_o} - k_{s_j} C_{p_j} - k_{r_j} C_{p_j} + k_{f_j} M_j C \tag{3}$$

in which

W_{p_j} = rate of mass input of the particulate adsorbed chemical of size fraction j, M/T

k_{s_j} = sedimentation coefficient of the j^{th} size fraction, T^{-1}

Summing the total over j size fractions or if only one size fraction is considered, equation (11) reduces to:

$$\frac{dC_p}{dt} = \frac{W_p}{V} - \frac{C_p}{t_o} - k_s C_p - k_r C_p + k_f MC \tag{4}$$

in which

k_s = overall sedimentation coefficient, T^{-1}

k_r = overall desorption rate constant, T^{-1}

k_f = overall adsorption rate constant, $L^3/M\text{-}T$

Adding Equations 2 and 4 cancels the adsorption and desorption terms and yields the rate of change of the total concentration C_T in terms of the dissolved and particulate:

$$\frac{dC_T}{dt} = \frac{W(t)}{V} - \frac{C_T}{t_o} - \Sigma kC - k_s C_p \tag{5}$$

in which

C_T = total concentration = $C + C_p$

W = total mass input

The sorption coefficients k_f and k_r are usually orders of magnitude greater than the decay and transfer coefficients of the dissolved and particulate phases. Thus instantaneous local equilibrium is achieved between the two phases - i.e. the rates of transfer and decay are so low that, comparatively, liquid-solid phase equilibrium is achieved very rapidly. The concentrations, C and C_p may be replaced by their equivalents in terms of C_T providing that the adsorption isotherm is known and that equilibrium is achieved. Linear adsorption isotherms have been reported elsewhere [6].

$$r = K_p \, C \tag{6}$$

in which

K_p = linear adsorption partition coefficient, $(M/M)/(M/L^3)$

r = amount of pesticide adsorbed per unit mass of dry sediment, M/M

It follows that C and C_p may be expressed in terms of C_T Under conditions of local equilibrium:

$$C = \frac{C_T}{(1 + k_p \, M)} \tag{7}$$

$$C_p = \frac{C_T \, K_p \, M}{(1 + K_p \, M)} \tag{8}$$

Substituting for C_p and C from the above relationships into Equation 5 the mass balance differential equation is:

$$\frac{dC_T}{dt} = \frac{W(t)}{V} - \frac{C_T}{t_o} - \frac{\Sigma k}{1 + K_p \, M} \, C_T - \frac{k_s \, K_p \, M}{1 + K_p \, M} \, C_T \tag{9}$$

which, under steady-state conditions may be expressed as:

$$C_T = \frac{W/V}{\frac{1}{t_o} + \frac{1}{1 + K_p M} \, [\Sigma k + K_p M k_s]} \tag{10}$$

Equation 9 is written for only one water compartment with sedimentation of suspended solids into the sediment compartment. It is straightforward to extend the analysis to a number of compartments (such as the lake configuration of Figure 2) with interflow and bulk dispersive transport between compartments. The equations are linear and may be solved analytically or numerically.

Bioaccumulation Model

The bioconcentration model follows the simple kinetics of Figure 3. The total pesticide concentration is the sum of the particulate plus the dissolved concentrations, with instantaneous sorptive equilibrium assumed. The total pesticide mass balance equation is identical to Equation 9 except it is written more concisely with fractions:

$$\frac{dC_T}{dt} = \frac{W(t)}{V} - \frac{C_T}{t_o} - (\Sigma k) f_1 \; C_T - k_s \; f_2 \; C_T \qquad (11)$$

in which

$$f_1 = \frac{C}{C_T} = \frac{1}{(1 + K_p \; M)} = \text{ fraction of dissolved pesticide}$$

$$f_2 = \frac{C_p}{C_T} = \frac{K_p M}{(1 + K_p \; M)} = \text{ fraction of particulate pesticide}$$

The mass balance for the concentration of pesticides tied up in fish biomass per unit volume of water, C_F, is:

$$\frac{dC_F}{dt} = k_1 \; f_1 \; C_T - k_d \; C_F \qquad (12)$$

in which

k_1 = biouptake rate constant, $\frac{\text{liters filtered}}{\text{kg fish-day}} \quad \frac{\text{kg fish}}{\text{liter}}$, T^{-1}

k_d = depuration rate constant, T^{-1}

$$k_d = \frac{k_1(\text{dissolved fraction})}{(\text{Biomass})\;(\text{Fish Partition})} = \frac{(k_1/\text{day})\;(f_1)}{\frac{(\text{kg fish})}{\ell}\;\frac{(\mu g/\text{kg})}{\mu g/\ell}}$$

If one divides Equation 12 by the fish biomass, a final bioaccumulation or fish residue equation results:

defining $\frac{dF}{dt} = (k_1 f_1 C_T/B) - k_d F$ (13)

F = whole body fish residue level, M/M wet weight

B = fish biomass concentration, M/L^3 wet weight

The bioconcentration factor (BCF) between pesticide residue in whole fish and the dissolved concentration is the ratio of the biouptake rate constant to the depuration rate constant divided by the fish biomass, $k_1/k_d B$. If pesticide is not metabolized in the fish, Figure 3 and Equation 13 are modified to reflect excretion of pesticide back into the dissolved phase.

Equations 11 and 13 may be solved analytically for constant coefficients and simple pesticide loading functions, W(t), or they may be integrated numerically. In the case of a pesticide ban, the W(t) might typically decline in an exponential manner due to degradation by soil organisms. For an expoentially declining loading function at rate ω, the analytical solutions to Equations 11 and 13 are:

$$C_T = C_{T_o} e^{-\delta t} + \frac{C_{Tin_o}}{\varepsilon} (e^{-\omega t} - e^{-\delta t}) \qquad (14)$$

$$F = F_o e^{-k_d t} + \frac{k_1 f_1}{B} \left\{ \frac{C_{T_o}}{\gamma} e^{-\delta t} + \frac{C_{Tin_o}}{\varepsilon\theta} e^{-\omega t} - \frac{C_{Tin_o}}{\varepsilon\gamma} e^{-\delta t} \right\}$$
$$- \frac{k_1 f_1}{B} e^{-k_d t} \left\{ \frac{C_{T_o}}{\gamma} + \frac{C_{Tin_o}}{\varepsilon\theta} - \frac{C_{Tin_o}}{\varepsilon\gamma} \right\} \qquad (15)$$

in which

C_{T_o} = initial total pesticide concentration in lake, ML^{-3}

C_{Tin_o} = initial total pesticide inflow concentration, ML^{-3}

ω = rate of exponentially declining inflow concentration, T^{-1}

$\alpha = (\Sigma k) f_1 + k_1 f_1 + k_s f_2$, T^{-1}

$\gamma = k_d - \alpha\ (1/t_o)$, T^{-1}

$\delta = \alpha + (1/t_o)$, T^{-1}

$\varepsilon = \alpha t_o + 1 - \omega t_o$, dimensionless

$\theta = k_d - \omega$, T^{-1}

The steady state solution to Equations 11 and 13 reduces to Equation 10 for the total pesticide concentration. For the fish residue level at steady state, the solution to Equation 13 simply yields the fish partition coefficient times the equilibrium dissolved pesticide concentration.

Multicompartment Solutions

Multicompartment solutions of Equations 11 and 13 must include interflows and bulk dispersion as well as an assumption regarding suspended solids and fish biomass distribution. For each constant volume compartment:

$$V \frac{dC_T}{dt} = \sum Q_a C_a - \sum Q_b C_T - k_{da} f_1 C_T V$$

$$- (k_s + k_{pa}) f_2 C_T V + k_{sa} f_2 C_a V_a + \frac{EA}{\ell} (C_a - C) \qquad (16)$$

where

V = compartment volume (m^3)

C_T = total pesticide concentration of the compartment ($\mu g/\ell$)

t = time (d)

Q_a = inflow of water from adjacent compartments (m^3/d)

Q_b = outflow of water to adjacent compartments (m^3/d

C_a = total pesticide concentration in the adjacent compartment ($\mu g/\ell$)

f_1 = fraction of the total pesticide in the dissolved phase

f_2 = fraction of the total pesticide in the particulate phase

K_{da} = reaction rate constant for the dissolved phase (d^{-1})

K_{pa} = reaction rate constant for the particulate phase (d^{-1})

k_s = settling rate constant of the compartment (d^{-1})

k_{sa} = settling rate constant from the above compartment (d^{-1})

E = bulk dispersion coefficient for adjacent compartments (m^2/d)

A = surface area between two adjacent compartments (m^2)

ℓ = mixing length between midpoints of adjacent compartments (m)

V_a = volume of above compartment (m^3)

The general mass balance equation for the compartments can be reduced to a general matrix equation, Equation 17.

$$\frac{d\{Cj\}}{dt} = \left[\frac{Q_{i,j}}{V_j}\right]\{C_i\} - \left[\frac{Q_{i,j}}{V_j}\right]\{C_j\} - \left[f_{1,j}\,K_{da} + f_{2,j}\,k_{s,j} + f_{2,j}\,K_{pa}\right]$$

$$\{C_j\} + \left[f_{2,i}k_{s,i}\;\frac{V_i}{V_j}\right]\{C_i\} + \left[\frac{E_{i,j}\;A_j}{\ell_{i,j}\;V_j}\right]\{C_i - C_j\} \qquad (17)$$

where i = subscript denoting adjacent compartments

j = subscript denoting the jth compartment

C_j = total pesticide concentration in a compartment ($\mu g/\ell$)

C_i = total pesticide concentration in an adjacent compartment ($\mu g/\ell$)

$Q_{i,j}$ = flow into compartment K (m^3/d)

$Q_{j,i}$ = flow out of compartment K (m^3/d)

$f_{1,j}$ = dissolved fraction of a pesticide in compartment K

$f_{2,j}$ = particulate fraction of a pesticide in comparmtnet K

K_{da} = sum of dissolved reaction rate constant (d^{-1})

K_{pa} = sum of particulate reaction rate constant (d^{-1})

$K_{s,i}$ = settling rate constant for compartment K (d^{-1})

$K_{s,j}$ = settling rate constant from an above compartment (d^{-1})

$E_{i,j}$ = bulk dispersion coefficient between adjacent compartments (m^2/d)

A_j = surface area of compartment K (m^2)

$\ell_{i,j}$ = length between the midpoints of adjacent compartments (m)

V_j = compartment volume (m^3)

V_i = volume of above compartment (m^3)

The equations comprise a set of linear, ordinary differential equations which were numerically integrated via a fourth order Runge-Kutta approximation technique.

RESULTS AND DISCUSSION

Fate and Transport The first step in fate and transport modeling is to determine the predominant reaction and transport pathways. Coralville is a short dentention time, flood control reservoir with a mean annual hydraulic detention time of only 14 days. This corresponds to a washout 0.0714 per day or approximately 7% of the dissolved material is exported through the outflow on an average day. Washout is expected to be a major transport mechanism in Coralville Reservoir. Other reaction rates and partition coefficients have been measured in laboratory studies and are summarized by pollutant in Table 2. Dieldrin should strongly adsorb to sediments and bioconcentrate, but degradation reactions are very slow. Furadan^R, a carbamate insecticide, is quite reactive, but biological degradation should predominate (Table 2). Selected herbicides and insecticides of usage in Iowa are listed in Table 2 with their laboratory protocol rate constant, half-lives, and partition coefficients.

The dieldrin time series of Figure 4 (dashed line) is from monthly grab sample data collected by The University of Iowa Hygienic Laboratory and indicates a steady decline in the envelope of peak concentrations during agricultural runoff events, as well as a decline in average annual concentrations. It is believed that the decline in dieldrin from the Reservoir outlet is due to the decreased aldrin application rates since 1967 as well as the microbial degradation of dieldrin by soil organisms on the land. Dieldrin loading rates in a small watershed runoff study from 1974 have been computed and range from 1.0×10^{-11} to 1.0×10^{-9} kg/m^2 - day, depending on the streamflow and hydrograph.

TABLE 2 PHOTOLYSIS, HYDROLYSIS, BIOLYSIS, AND SORPTION COEFFICIENTS FOR SELECTED IOWA PESTICIDES

	Near Surface Direct Photolysis		Alkaline Chemical Hydrolysis		Biolysis		Sediment/H_2O Partition Coeff.	Fish/H_2O Bioconcentration
	k_p, day^{-1}	$t_{1/2}$, days	k_B, $M^{-1}sec^{-1}$	$t_{1/2}$, days	$\frac{\hat{\mu}}{YK_M}$ $\left(\frac{\text{org-hr}}{l}\right)^{-1}$	$t_{1/2}$, days	$\frac{\mu g/kg \text{ dry}}{\mu g/l}$	$\frac{\mu g/kg \text{ wet}}{\mu g/l}$
Dieldrin	†	†			†	>10,000	10,000	10-100,000
DDT	†	†			†	†	100,000	130,000
DDE	0.7	1 [9]	~10^{-3}	1000 [10]	†	†	100,000	70,000
Carbofuran	0.003	~200 [11]	6×10^{-5}	>10,000 [11]	~10^{-11}	~3 [11]	500	~10
Fonofos, Thimet, Curbufos	†	†	10^{-4}	>365	4×10^{-10}	~9 [12]	200-500	
Atrazine	9×10^{-6}	81,000	10^{-16}	742 [13]	~10^{-11}	35	5-30	80
Cyanazine				>365	~10^{-11}	35	3-30	30
Alachlor				>365	~3×10^{-11}	12	50	~75
Trifluralin	0.03	22 [14]			†	†	500	1800-5800 [15]

†Denotes probable reaction of unknown rate

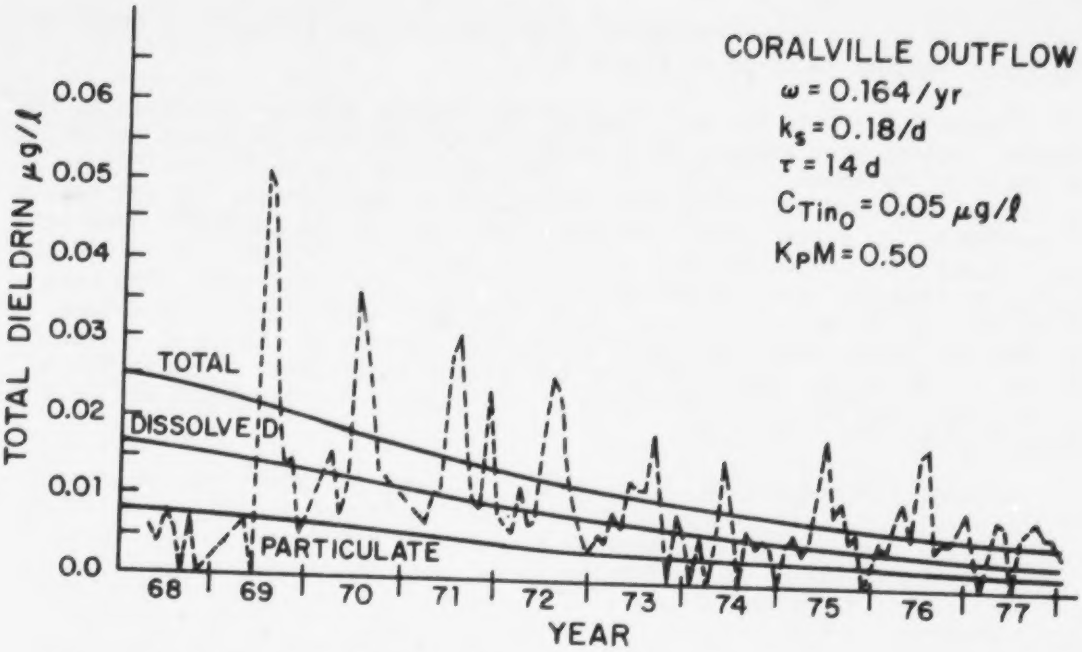


Figure 4. Model Results for Dieldrin Concentration in the Coralville Reservoir Outflow

Two Compartment Model The goal of this simulation was to analyze annual average concentrations, so transport properties (i.e., flow, volume, and sedimentation rate) were averaged over the period of simulation. A two compartment model as depicted in Figure 2 was utilized. Preliminary model results are presented for the Coralville Reservoir outflow in Figure 4. The dashed line in Figure 4 represents monthly grab sample field measurements, and the solid line is the annual average model simulation. Note the smooth decline in total and dissolved dieldrin concentrations due to an exponentially decreasing input loading function (Figure 5). The peak concentrations during runoff events recorded in the field data are not matched by the model results, since average inflow and a smooth loading rate function was assumed.

A sedimentation coefficient (k_S) of 0.18 per day was calculated from suspended solids removal rates in the Reservoir while a partition coefficient of 6250 µg/kg per µg/l (Kp) was estimated from field data [6]. The average suspended solids (M) in the reservoir from 1968-78 was 80 mg/l, so KpM was 0.50, indicating the ratio between the particulate and dissolved pesticide. Initially the total pesticide inflow concentration was 0.05 µg/l, but it was assumed to decline exponentially thereafter. The sum of the first order and pseudo-first order rate constants for dieldrin are believed to be quite small. The sum of the volatilization, biolysis, photolysis, and hydrolysis rate constants was assumed to be 1.7 x 10-4 per day or a half life of 11 years. At this rate, the decay reactions were insignificant compared to the transport and sedimentation of dieldrin. The pesticide is acting as an adsorbing, conservative substance and is tracking the input loading function of Figure 5.

Figure 6 presents the mass flux of particulate adsorbed dieldrin to the bottom. Solids were assumed to be permanently lost from the water column, so the model fails to include scour. Alternatively one could consider k_s to be an "apparent" or "effective" sedimentation coefficient, the net result of sedimentation minus scour. The mass transport to the sediments involves small quantities of pesticides, from 0.068 kg/day in 1968 to less than 0.014 kg/day in 1978, or about 46 percent of the total dieldrin input. The rate of decline in dieldrin transport to the sediment parallels, and is driven by, the declining input function. Sixty-four percent of the total dieldrin in the inflow to the reservoir model was in the particulate phase (KpM = 1.79). For a solids trap efficiency of 72% [20], a corresponding dieldrin removal of 46% was indicated.

A sensitivity analysis was performed in order to assess the importance of the partition coefficient and is presented in Figure 7. Figure 7 indicates that a several fold increase or decrease of KpM from 0.50 to 2.0 or 0.10, changes the total concentration by -47 and +49 percent respectively. The particulate fraction in Coralville Reservoir is only 33 percent of the total dieldrin if KpM is 0.50 (0.33 = (KpM)/(1+KpM)). Kellogg and Bulkey [1] indicated the same average in weekly samples from the Des Moines River, Iowa, during 1973.

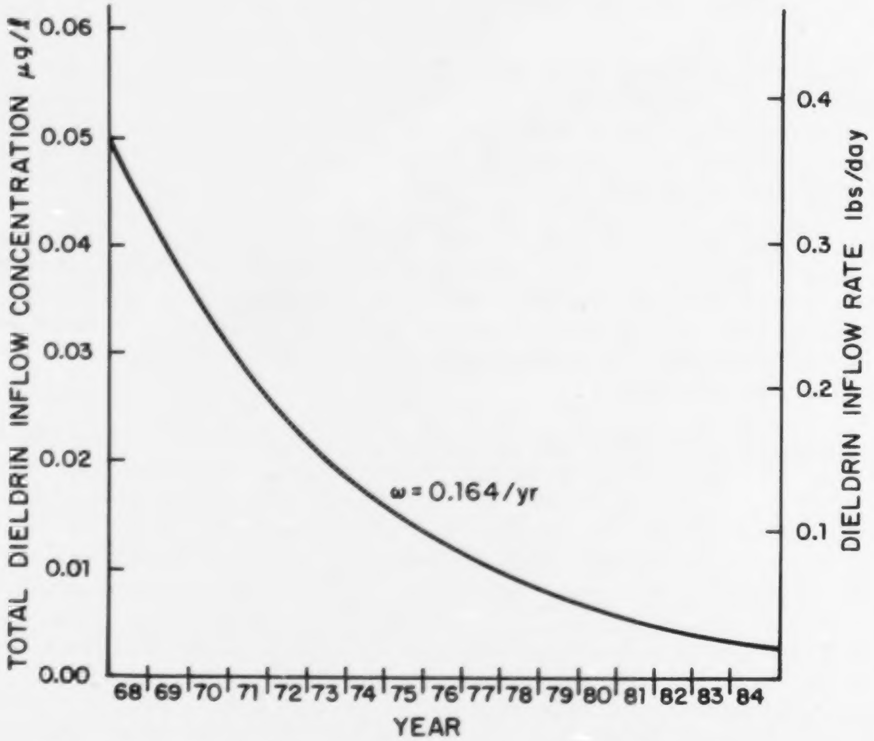


Figure 5. Input Loading Function to Coralville Reservoir

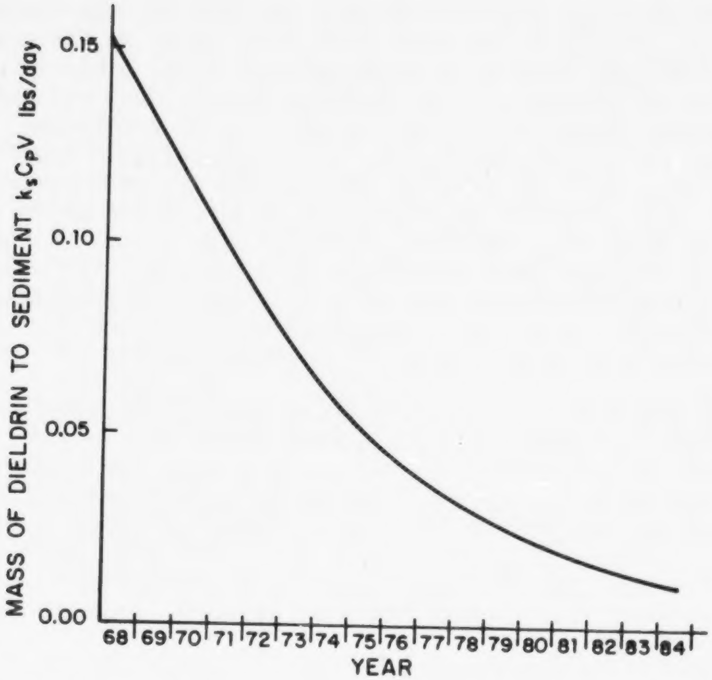


Figure 6. Calculated Mass Flux of Dieldrin to the Sediment

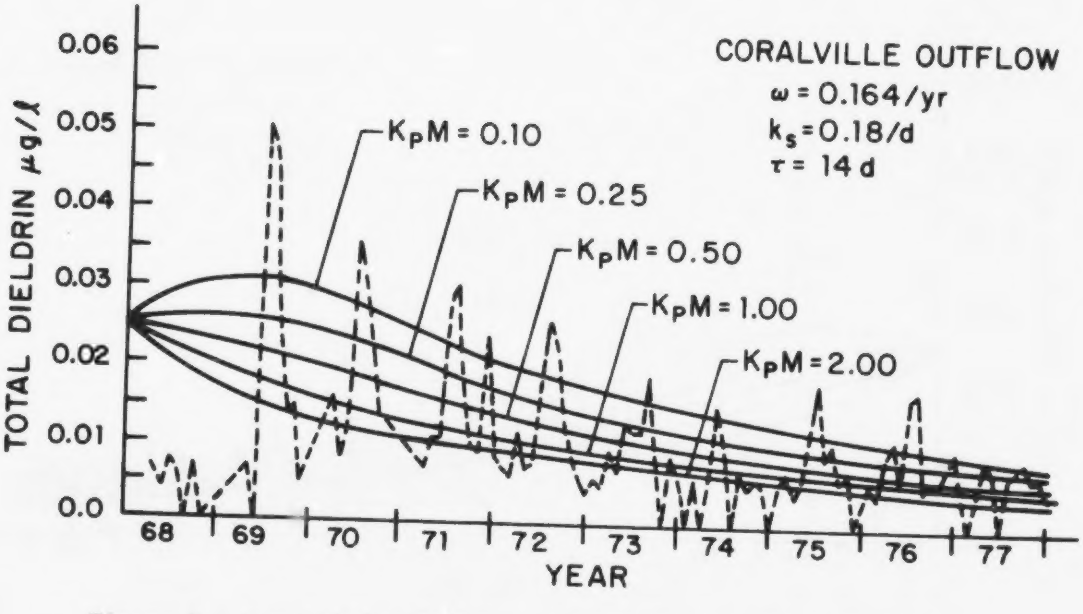


Figure 7. Sensitivity Analysis of the Effect of the Partition Coefficient, K_p

The sedimentation coefficient (k_s) also affects the dieldrin removal by sedimentation. Figure 8 indicates that an increase of the coefficient from 0.18 to 0.28 per day results in a decrease of total dieldrin of 30 percent. The mass flux of dieldrin to the sediment (k_sC_pV) does not fully double when the sedimentation coefficient doubles due to a decreased particulate concentration in the reservoir, C_p. This sedimentation coefficient corresponds to a settling velocity of k_s times the mean reservoir depth, or 0.44 m/day. The geometric mean diameter of a particle which settles at 0.44 m/day is about 3μm, the fine silt/clay size range. Although size distributions have not been determined for particles within Coralville Reservoir, the mean particle size of the inflow is approximately 15 μm, a silt size classification. It is expected that the mean particle size of the inflow should be greater than the mean size within the Reservoir.

Results presented in Figures 4-8 did not include biological uptake by fish. Figures 9 is identical to Figure 4 except for including the effects of biological uptake and metabolism. Fish biomass and productivity in Coralville Reservoir is extremely large, estimated at 1,000 lb/acre (0.11 kg/m^2) (46 mg wet weight per liter at conservation pool). Although the fish biomass is large, the decrease in total dieldrin concentration due to uptake by fish was less than 0.002 μg/l after 10 years of simulation. This fact is attributed to the rapid rates of pesticide washout and sedimentation in Coralville Reservoir.

Figure 9 presents the model results and field data for dieldrin residues in sediment and the edible tissue of bottom feeding fish in Coralville

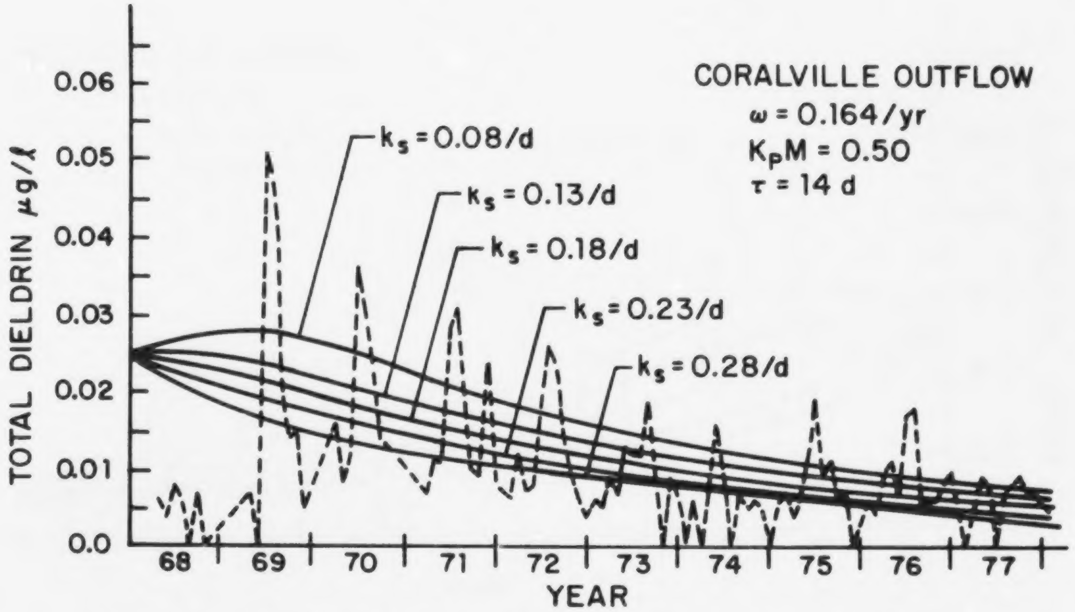


Figure 8. Sensitivity Analysis of the Effect of the Sedimentation Coefficient, K_s

Reservoir. Fish taxa include bigmouth buffalo, carp, carpsucker, catfish, and channel catfish. Fish were collected by shocking and were subsequently filleted and analyzed [21, 22, 23]. Model coefficients included:

$k_1 = 0.027/\text{day}$	uptake rate constant
$k_d = 0.0083/\text{day}$	depuration rate constant

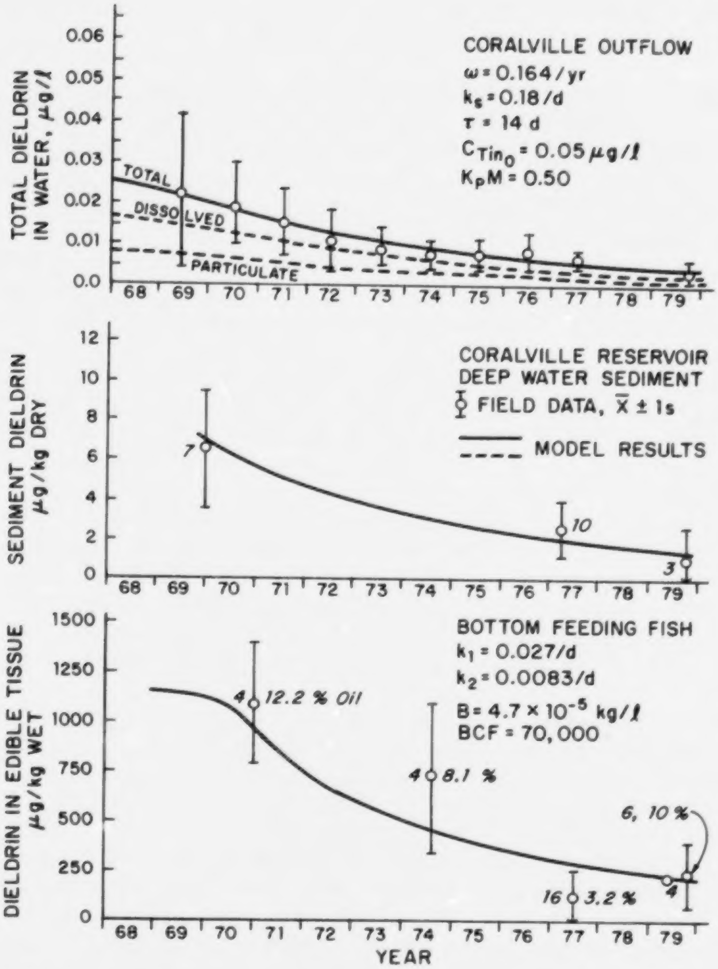


Figure 9. Field Data and Model Results for Dieldrin in Coralville Reservoir. Numbers represent the number of data points and percentages are the percent oil or lipid content of the catch.

$B = 4.67 \times 10^{-5}$ kg/l biomass concentration

$F_o = 1150$ μg/kg initial whole body residue

$k_2 = 0.005$/day sediment biological degradation

A total of 1.4 percent per day of the dissolved pesticide is filtered by bottom feeding fish. The rate constants are in relative agreement with those of Thomann [24]. The effective fish filtration rate was 600 liters filtered per kg of wet fish per day and was utilized in the estimation of k_1. The partition coefficient between fish and water was estimated from field data to be 70,000 μg/kg per μg/l. Note that this is more than ten times the equilibrium partition coefficient for dieldrin between suspended solids and water. Dieldrin concentrates in bottom feeding fish due to large uptake and relatively small depuration rates.

The sediment compartment receives the mass flux of dieldrin depicted in Figure 6 due to sedimentation. The mass of dieldrin in the sediment is strongly partitioned into the particulate phase by adsorption. The ratio of particulate dieldrin to dissolved dieldrin is equal to KpM or approximately 2,000, assuming a solids concentration in the sediment of 0.32 kg/ℓ. The decline in sediment concentration follows the declining mass input rate to the sediment (Figure 6), but it also biodegrades at a rather slow rate of ∿0.005 per day. Biodegradation in the sediment compartment is assumed to occur for both dissolved and particulate dieldrin.

Bioconcentration of hydrophobic pesticides in Coralville Reservoir fishes is directly proportional to the oil or lipid content of the catch. By normalizing all of the fish residue data on an oil basis, it is possible to use Equations 12 and 13 to simulate all taxa of fish simultaneously. The oil content is the fraction of the total wet weight which is extractable with petroleum ether. Figure 10 presents results for all fishes in which a measurement of oil content was performed. While the data are sparse, it appears that such a simple bioconcentration model has validity. The only difference between the simulations depicted in Figures 9 and 10 is the biomass (wet weight vs. oil) and the corresponding BCF factor (in fish flesh vs. oil). The uptake and depuration rates remain constant.

The results of Figures 9 and 10 indicate that the average catch no longer exceeds the FDA action level of 300 μg/kg residue. Uptake by fish accounts for almost 10% of the inflow dieldrin loading, while ∿42% of the inflow undergoes sedimentation to the bottom of the reservoir, and 48% is exported through the outflow. The partitioning of dieldrin in the water column is 64% in the fish, 24% dissolved in the water, and less than 12% adsorbed to suspended solids. Sediment and fish (and fish oil) are essentially in equilibrium with mean dissolved dieldrin concentrations. If biouptake is ignored in the model or if depurated dieldrin is not metabolized but rather returned to the dissolved phase, then the transport in the outflow is 54% and the net sedimentation is 46% of the total dieldrin load.

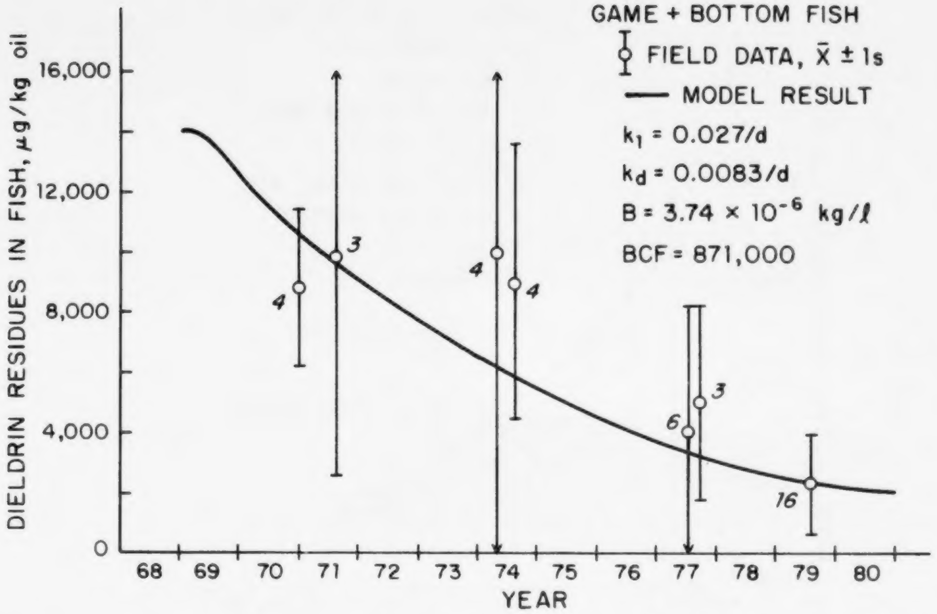


Figure 10. Field Data and Model Results for Dieldrin in Coralville Reservoir Fish, Normalized on an Oil Basis.

Eight Compartment Model Results of the eight compartment model are presented in Figures 11 and 12. Field data were not available for each compartment. The field data of Figure 11 is downstream from the Reservoir at Iowa City and most closely represents the hypolimnion compartment 6 and the epilimnion compartment 3. There appears to be good agreement between model results and field observations.

The addition of compartments to the model provides insight into the dynamics of dieldrin transport, scour, and deposition. The only difference between the two compartment and the eight compartment model was that a small amount of scour was introduced into the sediment compartment, resulting in a lower net sedimentation rate. Compartmentalization of the system roughly offset this effect. Resulting dieldrin concentrations in the dissolved, particulate, and sediment phases all decreased proceeding downstream through the Reservoir, a result of sedimentation from the water column of a progressively lower particulate dieldrin concentration. A check on the mass balance of solids in the reservoir model indicated that sedimentation was greater than scour, which is also true of the prototype system. Scour of dieldrin from the sediment to the water was a small but significant contribution to the mass balance at the sediment-water interface. Bulk dispersion coefficients in the vertical and longitudinal directions were 9.3×10^{-4} and 4.6×10^{-4} m^2/d, respectively, with a dispersive scour at the sediment-water interface of 1.5×10^{-4} m^2/d.

The addition of compartments to the model is not an arbitrary choice. It should reflect the physical geometry of the prototype and/or the

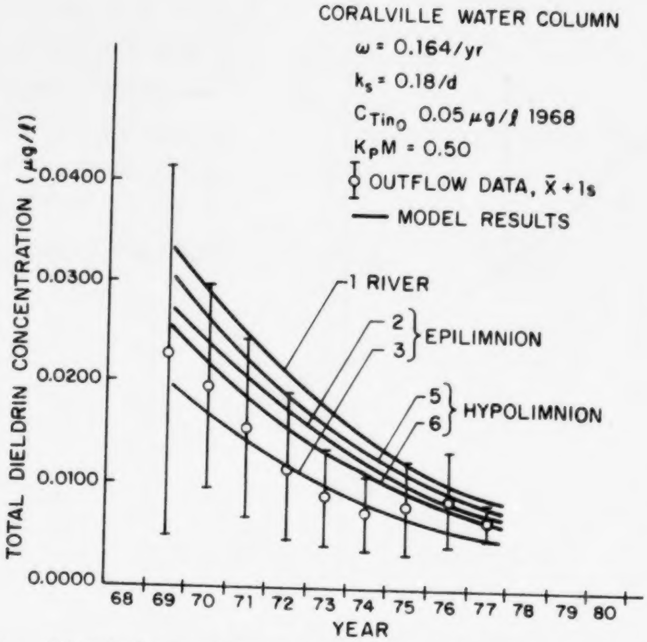


Figure 11. Eight Compartment Model Results for Dieldrin in the Water Column.

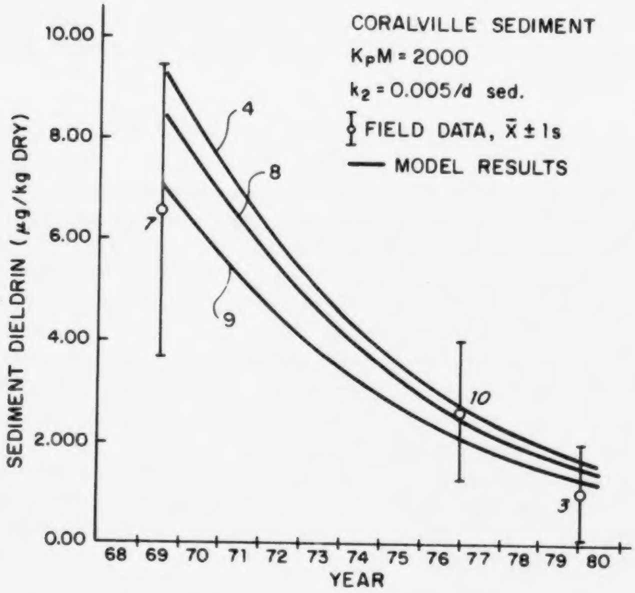


Figure 12. Eight Compartment Model Results for Adsorbed Dieldrin on the Sediment

estimated dispersion pattern. Assuming a longitudinal dispersion coefficient of $\sim$4 mi^2/day, it is possible to estimate the proper number of longitudinal compartments necessary to reflect this degree of dispersion. For Coralville Reservoir, approximately 10 reactors in series would be required disregarding any bulk dispersion between compartments. As you increase the number of compartments, the model becomes more "plug-flow" in nature. Since a greater amount of material will settle out in a "plug flow" system, it would be necessary to decrease the sedimentation rate constant to reflect the field data.

Unsteady Flow Simulations

Errors are generated in the annual average, steady flow simulations (Figures 4-12). Mass fluxes are underestimated by using annual average flowrates and calibrating the model output with annual average water concentrations. For this reason an unsteady flow simulation was performed for dieldrin in Coralville Reservoir during 1976. Inflow and outflows are shown in Figure 13. Note that the Reservoir volume was drawn-down from February - May and subsequently refilled. Input of dieldrin was unmeasured, so this calibration involved fitting the measured output dieldrin concentration by adjusting the inflow concentration (Figure 14). Mass flux to the sediment (Figure 15) is approximately 20% larger than that of the steady flow results if they are run with comparable input loadings. Such errors would be even larger for simulations with time variable loadings of suspended solids.

If the goal is to accurately reflect mass fluxes of sediment and dieldrin, then one must use a fully time variable approach. If annual average exposure concentrations are all that is required, then a steady flow approach similar to Figures 4-12 is warranted.

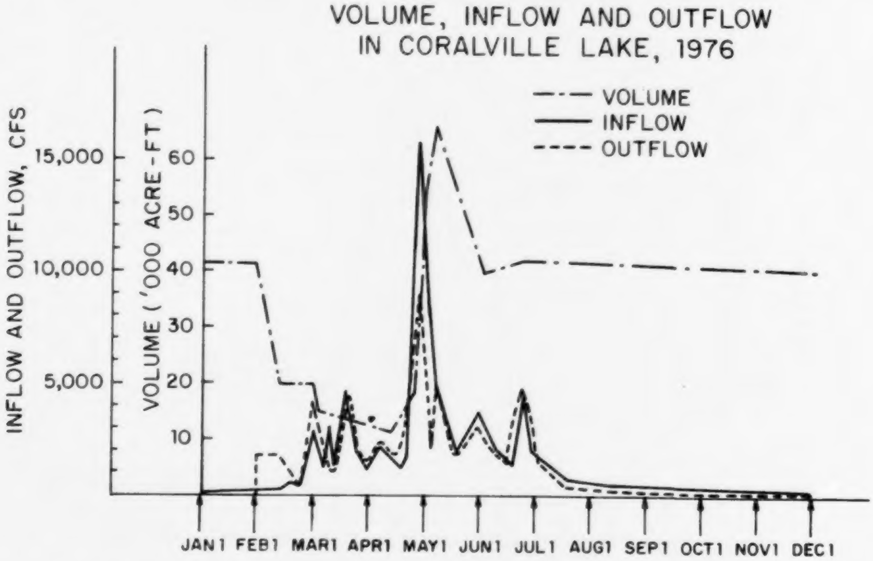


Figure 13. Unsteady Flow Simulation

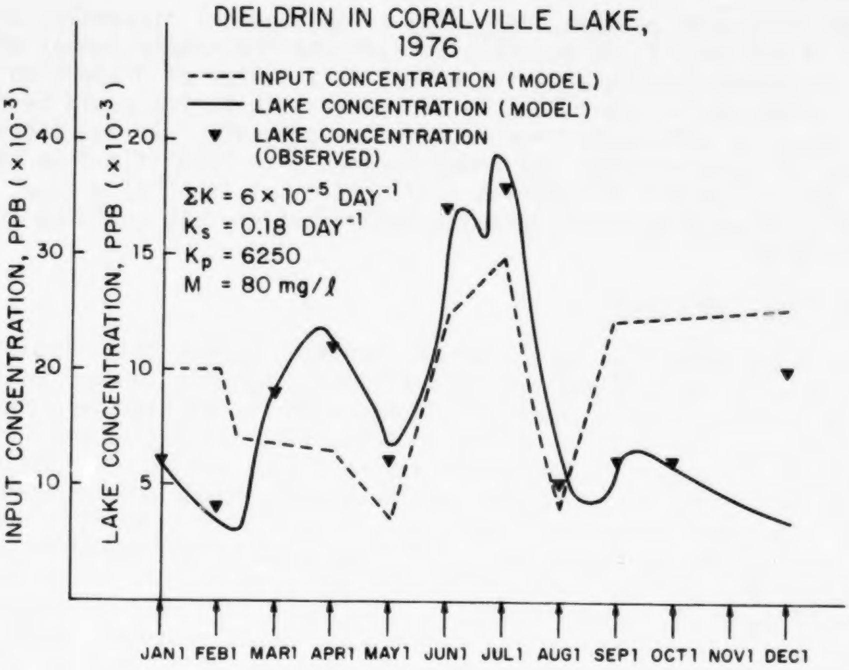


Figure 14. Unsteady Flow Results

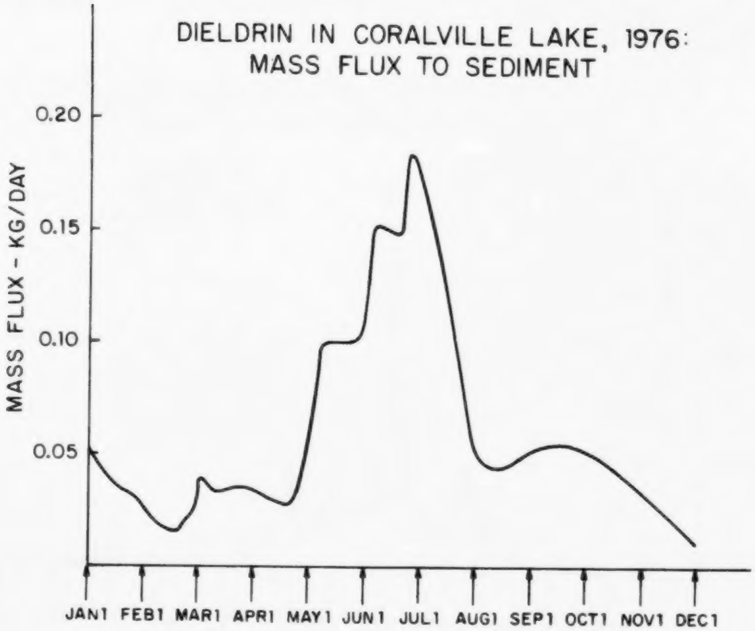


Figure 15. Unsteady Mass Flux to the Sediment

The mass flux to the sediment shown in Figure 15 provides information about seasonal variations that is not possible with annual average simulations. It has been observed that fish, especially bottom feeding fish, reach peak residue levels of dieldrin and other insecticides in June. This is due to higher dieldrin concentrations in the water as well as more recently contaminated sediment following spring runoff.

Historical Sediment Profiles

Sediments are historically contaminated with dieldrin, but the degree of contamination has decreased since the ban in 1975. A typical upstream sediment core is shown in Figures 16 and 17.

In sandy substrates, such as the inflow delta, finer material is deposited near the surface of the sediment under low flow, ice-covered conditions. This fine silt is characterized by high organic content and volatile solids greater than 10%. In these locations one observes a maximum dieldrin concentration in surficial sediments (Figure 16). The bed is continuously being reworked each year, and the fine silts will be subsequently scoured, resuspended, and deposited downstream. An interesting feature of Figure 16 is the relatively constant sediment concentration with depth on a volatile solids basis. There are some indications that the sediment is disturbed enough to create rather uniform concentration profiles on a volatile solids basis. This could indicate thermodynamic equilibrium is achieved in mixed sediments.

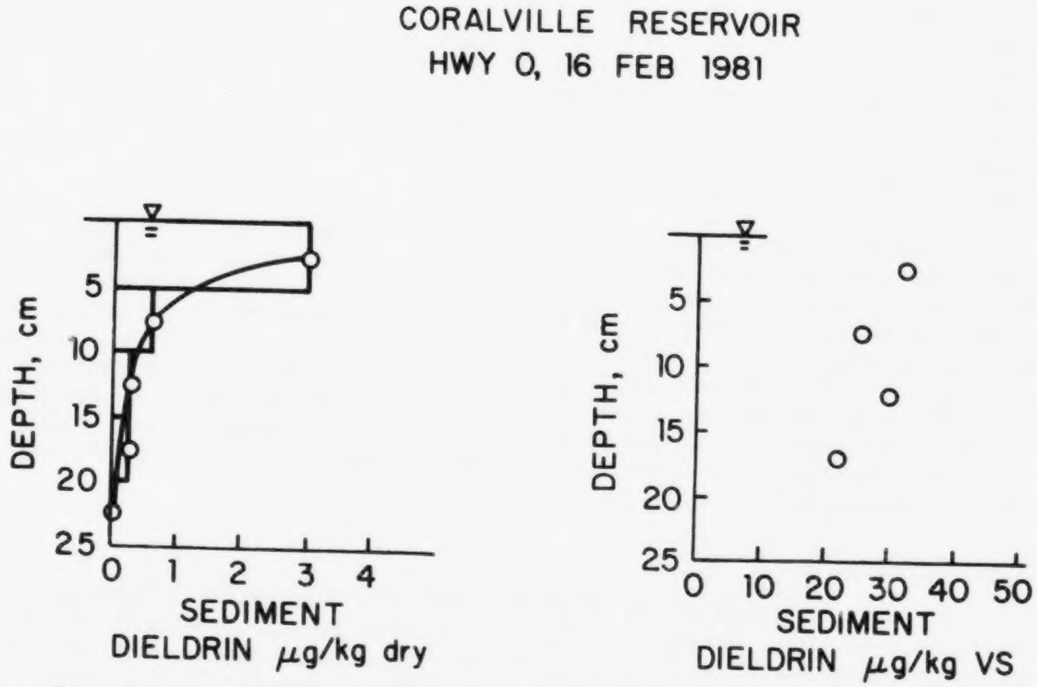


Figure 16. Sediment Core Near the Inflow to Coralville Reservoir

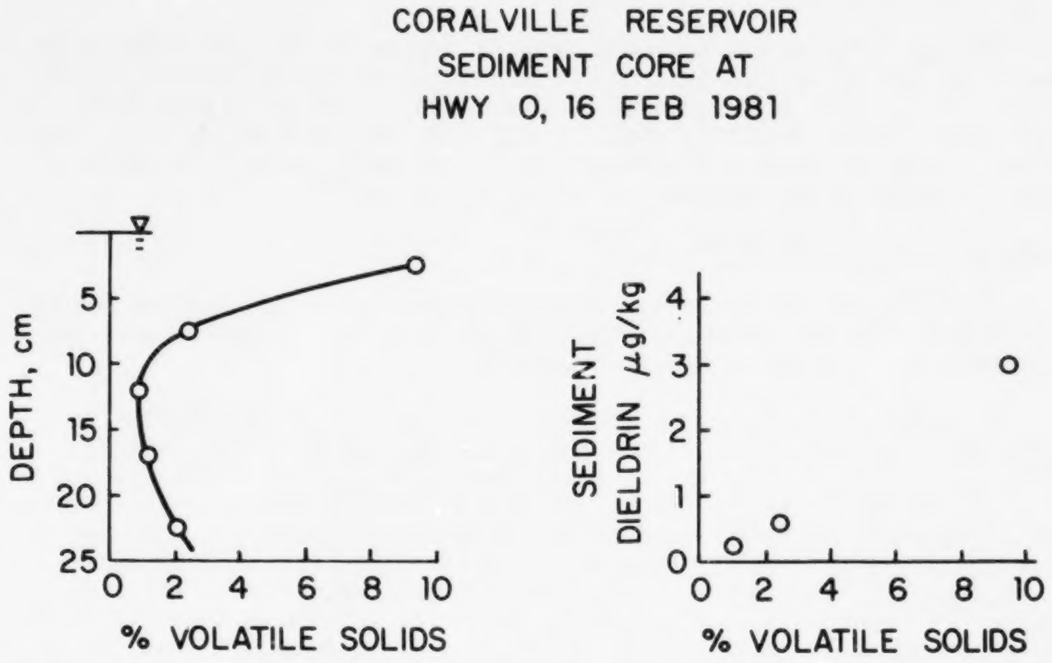


Figure 17. Volatile solids in the Sediment Core Relationship

A point in contrast is the sediment concentration profiles in highly depositing basins of the Reservoir. Figure 18 has been constructed from field data and model simulations using sediment layers of ~6 cm depth. In Coralville Reservoir, the annual average deposition is 5.8 cm/year. A twenty year scenario is depicted in Figure 18 which shows the dieldrin concentration on suspended particulate materials reaching a peak concentration in the late 1960's and then declining.

In depositional zones, the high rate of sedimentation of cohesive sediments precludes a great degree of mixing. Field data, although it is very sparse, supports the conclusion that some degradation of dieldrin is occurring in the sediment -- otherwise sediment concentration profiles would be considerably larger. Interstitial waters track the sediment concentration very well. Diffusion and sorption of dissolved dieldrin to the sediment from the water column may occur if sediment degradation reactions decrease sediment and interstitial concentrations as shown. Otherwise the sediments serve as a source of dieldrin to the water column by scour/resuspension, and desorption/diffusion.

Bioconcentration

The total storage of dieldrin in Coralville Reservoir is largely in the sediment (~45 kg). Bottom feeding fish contain perhaps 0.5 Kg while the water column contains only ~0.2 kg and particulate suspended material ~0.1 kg. All other elements of the ecosystem contain very little dieldrin.

Apparently biomagnification is not a large problem since bottom feeding fish have the highest biomass and residue levels (Figure 19).

There exists a strong correlation between insecticide residue levels in fish and the percent oil or fat (petroleum ether extraction). To demonstrate that the residue level of fish is directly related to their fat (oil) content, Figure 20 was plotted with 1979 data for a variety of fish species and seasons. Fish samples were analyzed according to US FDA procedures by the University of Iowa Hygienic Lab. Figures 20 demonstrates that oil content removes ~60% of the variance (r^2) in fish residue samples regardless of fish species. Autumn (October-November) residues in fish are lower than summer (June and August) samples, primarily due to a difference in exposure concentrations from agricultural runoff.

The slope of the line in Figure 20 gives the residue level in fish oil at the 1979 exposure levels. The annual average insecticide exposure con-

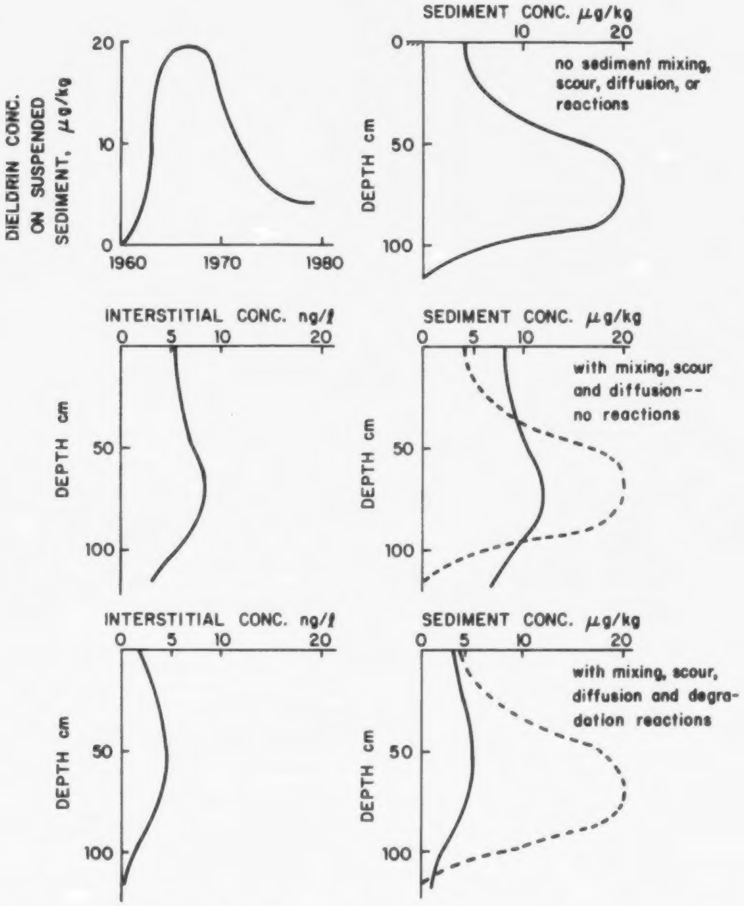
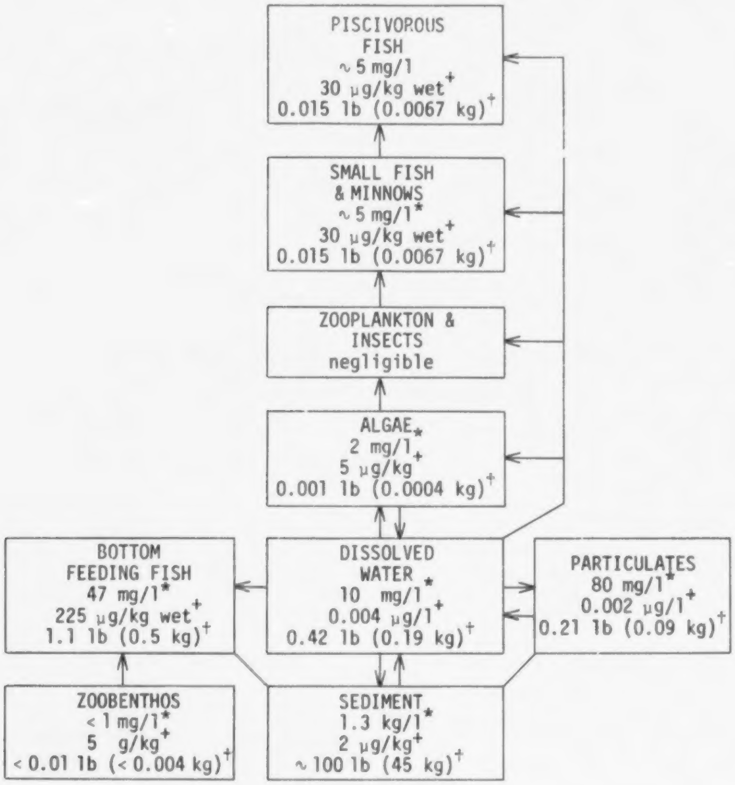


Figure 18. Estimated Dieldrin Sediment Concentrations and Loading Scenario in Highly Depositional Zones of Coralville Reservoir

centrations during this period were 0.0045 μg/l dieldrin, ∿ 0.002 μg/l chlordane (cischlordane plus trans-chlordane plus nonachlor), ∿ 0.001 μg/l DDE, and ∿ 0.001 μg/l heptachlor epoxide. Based on this residue and exposure data, the oil-normalized bioconcentration factors (BCF-oil) expressed as $\log_{10}$ BCF μg/kg oil per μg/l are 5.7, 6.0, 5.9, and 5.8 for dieldrin, chlordane, DDE, and heptachlor epoxide respectively. Figure 21 shows the log BCF-oil plotted for a number of insecticides in Iowa waters. Oil-normalized BCFs correlate with the octanol water partition coefficients.

Alachlor in Lake Rathbun

Field data on alachlor was gathered on Lake Rathbun, a south-central Iowa reservoir on the Chariton River, by the University of Iowa Hygienic Laboratory. The study was conducted during a high flow runoff period. Under these conditions, Lake Rathbun had a mean depth of approximately 29 feet, a


PISCIVOROUS FISH
∿ 5 mg/l
30 μg/kg wet+
0.015 lb (0.0067 kg)†
SMALL FISH & MINNOWS
∿ 5 mg/l*
30 μg/kg wet+
0.015 lb (0.0067 kg)†
ZOOPLANKTON & INSECTS
negligible
ALGAE*
2 mg/l+
5 μg/kg
0.001 lb (0.0004 kg)†
BOTTOM FEEDING FISH
47 mg/l*
225 μg/kg wet+
1.1 lb (0.5 kg)†
DISSOLVED WATER
10 mg/l*
0.004 μg/l+
0.42 lb (0.19 kg)†
PARTICULATES
80 mg/l*
0.002 μg/l+
0.21 lb (0.09 kg)†
ZOOBENTHOS
< 1 mg/l*
5 g/kg+
< 0.01 lb (< 0.004 kg)†
SEDIMENT*
1.3 kg/l*
2 μg/kg+
∿ 100 lb (45 kg)†

---

[*] BIOMASS

[+] DIELDRIN CONCENTRATION

[†] DIELDRIN MASS

Figure 19. Biomass, Dieldrin Concentration, and Dieldrin Mass in Coralville Reservoir Ecosystem, 1980

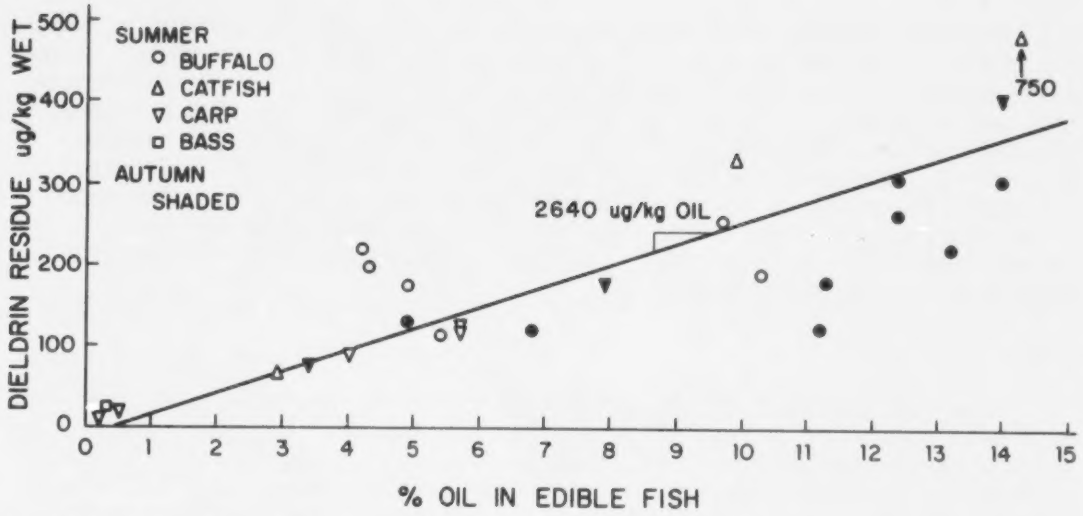


Figure 20. Dieldrin Residues in Fish vs. Percent Oil Content, Coralville Reservoir, 1979 Field Data. Equations for least squares regression: Y = 2640, X -10.8, r = 0.77.

mean hydraulic detention time of 162 days, and a mean volume of 4.33 x 10^8 cu. meters. Rathbun's 535 square mile watershed is primarily in row crop agriculture and pasture land. Grab samples were collected from four locations representing the two principal inflows from the Chariton River and South Chariton River, a depth composite sample from Lake Rathbun, and a downstream sample. Weekly samples of water, fish, and sediment were collected.

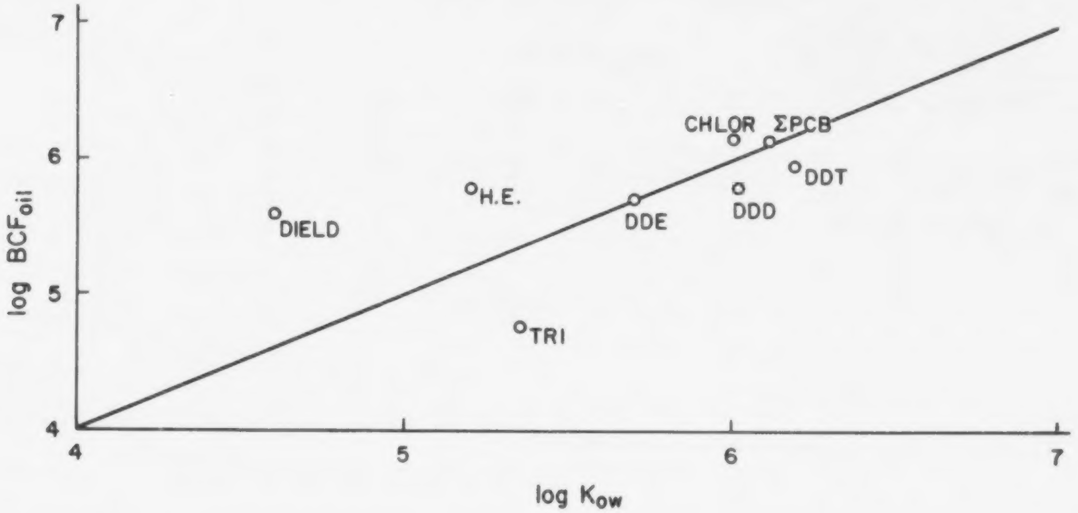


Figure 21. Field Bioconcentration Factors in Fish Oil vs. Octanol/Water Partition Coefficients. DIELD = dieldrin, H.F. = heptachlor epoxide, TRI = trifluralin, CHLOR = chlordane

Modeling efforts on Rathbun Reservoir in Iowa for the herbicides alachlor and atrazine are much different than for hydrophobic pollutants. Being quite soluble, these herbicides are shown to undergo negligible sedimentation but to biologically degrade and to be transported out of the Reservoir via the outflow. Figures 22-25 are the results for alachlor in Rathbun Reservoir. Time-variable loadings and flow were required to accurately calibrate the model to in-situ and outflow concentration data. The rate of degradation was significant, and pseudo-first order rate constants ranged from 0.03 - 0.05 per day, in relative agreement with laboratory biotransformation measurements.

CONCLUSIONS

Fate and transport of the pesticides dieldrin, alachlor, and atrazine have been simulated in Coralville and Rathbun Reservoirs, Iowa. The soluble herbicides alachlor and atrazine have been shown to biologically degrade and to be transported out of the Reservoirs in the outflow. Their rate of degradation is significant, and first order biodegradation rate constants range from 0.02-0.06 per day.

From the dieldrin analysis it was determined that 40% of the dieldrin inflow to Coralville Reservoir is lost to the bottom via sedimentation and 50% is released through the dam gates of this short detention time Reservoir. Uptake by fish accounts for about 10% of the dieldrin input due to the extremely large biomass of biota, 1000 lb./acre. The partitioning of dieldrin in the water column is 64% in the fish, 24% dissolved in the

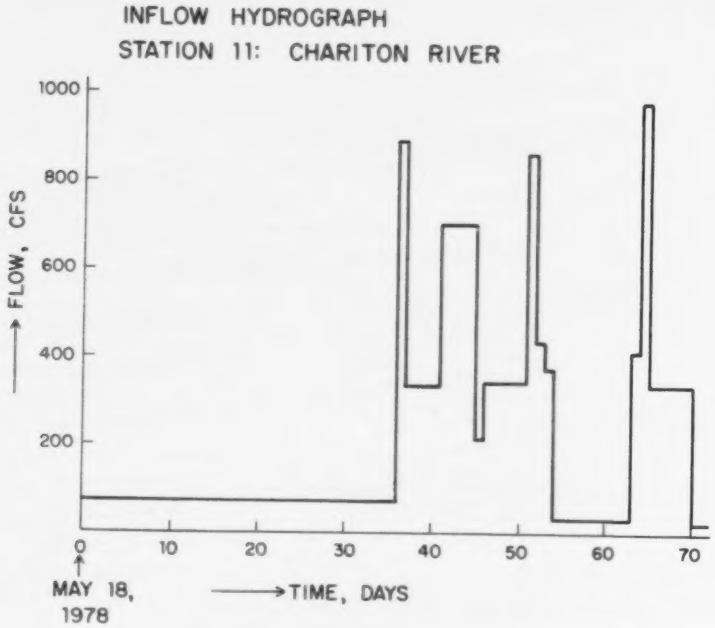


Figure 22. Inflow to Rathbun Reservoir from the Chariton River

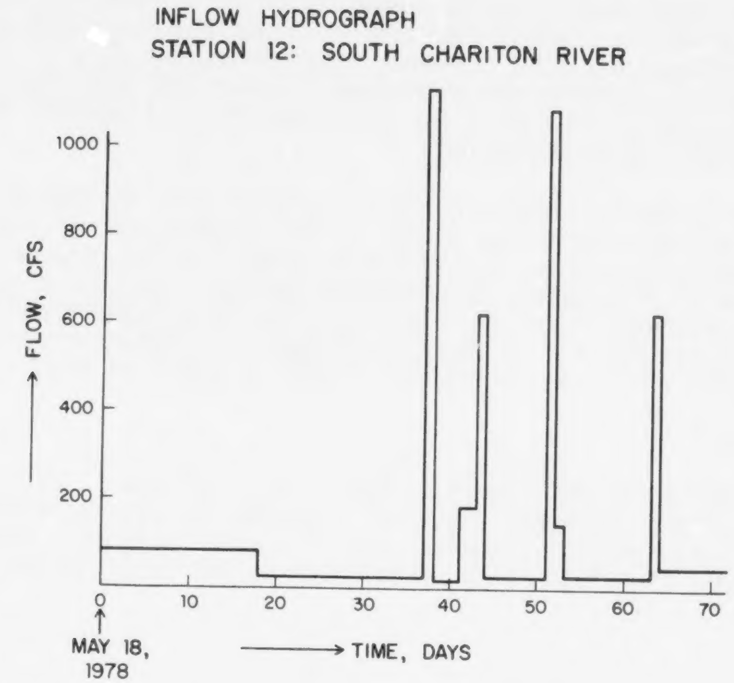


Figure 23. Inflow to Rathbun Reservoir from the South Chariton River

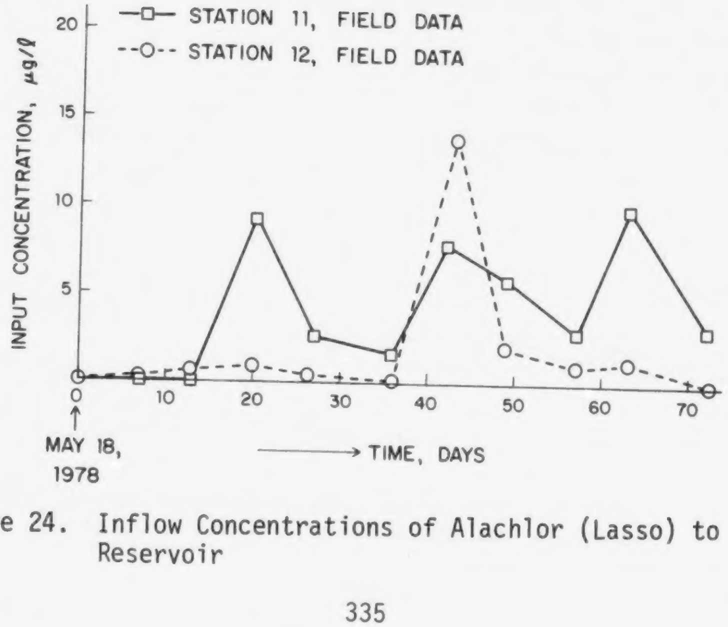


Figure 24. Inflow Concentrations of Alachlor (Lasso) to Rathbun Reservoir

water, and less than 12% adsorped to suspended solids. Mean residues in the edible tissue of bottom feeding fish have declined below the FDA guideline of 300 PPB. Fish and sediment concentrations are essentially in equilibrium with mean dissolved dieldrin concentrations. Under low flow conditions, the sediment becomes a net source for pesticide in the Reservoir via desorption and pore water diffusion.

Field monitoring of bioconcentration factors (BCF) in fish indicated that residues are directly proportional to fat content and dissolved exposure concentration alone, regardless of diet, species, sex, weight, length, portion of fish taken, or condition factor. For this situation field BCFs corresponded quite closely with laboratory measurements when normalized on a fat basis. In fact normalized field BCFs corresponded to the octanol-water partition coefficient within a factor of ten.

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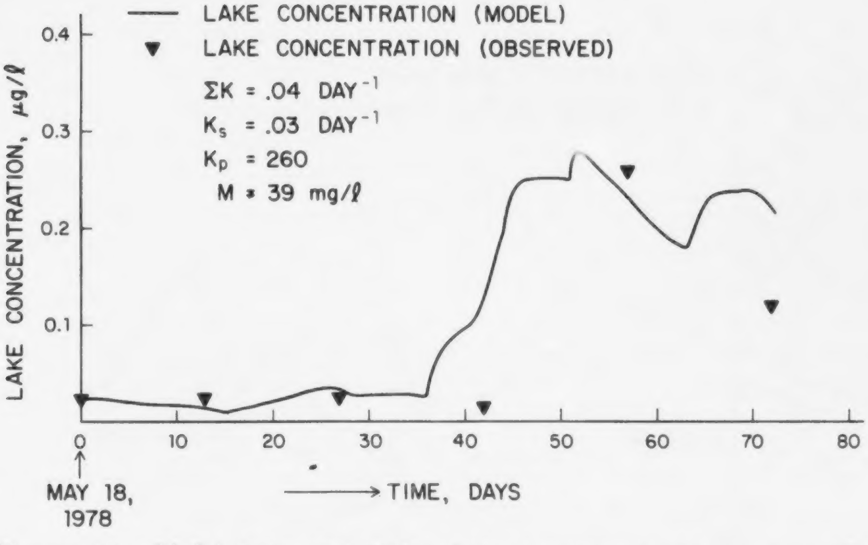

Figure 25. Field Data and Model Output Concentrations from Rathbun Reservoir for the Herbicide Alachlor (Lasso)

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This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication.

TECHNIQUE FOR PREDICTING RIVER WATER POLLUTION BY DDT AND γ-BHC RESIDUES DURING SPRING FLOODS

by

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At present, despite the ban on DDT use in a number of developed countries, there exists a problem of global pollution of the biosphere by this and other organochlorine pesticides (OCP).

This is associated with the fact that OCP are persistent toxicants which can be found almost in all natural environments for a long time after their application.

In addition, some developed countries still produce pesticides, DDT included, on a large scale and export a considerable part of their production to other countries (12).

As a result of the atmospheric circulation, pesticides evaporated from the soil are transported all over the world (11) and found where they have never been applied (13).

A main route of the entry OCP into rivers is their washout from a watershed in surface slope runoff waters (1,7) formed as a result of snow melting and rainfall.

Watershed pollution by OCP is caused by their residues in soils and cumulative build-up of precipitation from the atmosphere.

The highest concentrations of OCP in river waters and watercourses were observed during the period of surface runoff (3,2).

Surface runoff of pesticides depends on many factors, the main of them being, apparently, solubility, conditions of water runoff, the caracter of pesticide distribution over a watershed and erosion properties of soil.

The latter factor is especially important when pesticides are transported by runoff on soil particles (10).

Water runoff makes possible the migration of pesticides and soil particles passed into the solution, thus being the determining factor for their washout from a watershed.

Maximum surface water runoff from watersheds of the lowland rivers in the European part of the Soviet Union typically occurs in spring.

During this period the water runoff of the rivers is formed mainly due to the entry of melt waters from a watershed into a river bed (70-90%) (6).

Therefore, river water pollution by DDT and γ-BHC in the above-mentioned rivers in spring will be determined mainly by the content of pesticides in slope waters flowing down from the watershed.

The amount of pesticides entering the river bed during the period of slope runoff is

$$u_i = f_i N_i, \qquad [1]$$

where N_i is the amount of the i-th pesticide accumulated in the watershed by the time of snow melting;

f_i is the portion of the pesticide entering the river bed, or the runoff coefficient of the i-th pesticide.

In this case, the average flood-period concentration of the i-th pesticide in the outlet (closed to the river mouth) observation point of the watershed will be

$$\bar{C}_i = \frac{u_i}{W}, \qquad [2]$$

where W is the volume of water runoff during the flood period in the outlet observation point.

Expressing W as

$$W = k\, W_{slope}, \qquad [3]$$

where W_{slope} is the volume of slope waters arriving from the watershed and k is the factor of proportionality between the water runoff of the river in the outlet observation point and the slope runoff ($k \geq 1$), we obtain

$$\bar{C}_i = \frac{f_i\, N_i}{k\, W_{slope}} \qquad [4]$$

The amount of pesticides accumulated in the watershed N_i and the runoff coefficient f_i of DDT and γ-BHC are determined experimentally, whereas the volume of water runoff is predicted.

The storage of DDT and γ-BHC in the watershed before the beginning of snow melting is the sum of their amount accumulated in the snow cover and soil.

Pesticide storage in snow cover is determined before the beginning of snow melting, and that in soil prior to the snowfall.

It should be noted that while determining the storage of pollutants in the soil of a watershed for predicting the pollution of river waters, one encounters the element of uncertainty.

As we discussed earlier (7,8), this uncertainty is associated with a choice of the required depth of soil layer where the storage is to be assessed.

The runoff coefficient of DDT and γ-BHC was determined experimentally on real river watersheds and runoff plots (4,7, 9).

We determined the storage of DDT and γ-BHC in the snow cover of a given watershed or runoff plot, their storage in the 0-20 cm layer and their washout from these watersheds in runoff water.

The runoff coefficient of DDT and γ-BHC can be expressed in fractions of both the total storage and the storage in snow cover alone.

The coefficient f_i obtained under natural conditions actually reflects the process of pollution formation of melt waters flowing down from the watershed by DDT and γ-BHC residues, and also due to the underlying surface of the watershed.

The studies conducted showed that the runoff coefficient of pesticides is directly proportional to the volume of water runoff, as are the previously obtained runoff coefficients of other ingredients (5,9):

$$f_i = f_i' y^n , \qquad [5]$$

where y is the volume of waters flowing down from the watershed which is expressed in terms of the runoff layer ($y = \frac{W_{slope}}{F}$, F - the area of watershed).

Index n is close to unity, and to a first approximation, the relationship may be assumed to be linear.

In this case, proportionality factor f_i' is the normalized, or reduced, runoff coefficient [5] which characterizes a relative washout of the i-th pesticide from the watershed with a layer of water runoff 1 mm.

Substituting [5] in [4] gives

$$\bar{C}_i = \frac{f_i' N_i}{kF} \qquad [6]$$

The value of the reduced runoff coefficient for DDT and γ-BHC is $1 \cdot 10^{-2}$ and $7.9 \cdot 10^{-3}$, respectively (taking no account of the storage of pesticides in soil), or $2.3 \cdot 10^{-5}$ and $4 \cdot 10^{-5}$, respectively (taking into account the storage of pesticides in the 0-20 cm soil layer).

These values were obtained for a water content varying in the range from 0.34 to 75 mm.

According to the observations of many years, the value of water runoff for the rivers of the territory under study varies in this range.

Consequently, the obtained runoff coefficients of pesticides can be applied to the rivers in the middle zone of the European part of the Soviet Union.

The technique considered was used for predicting the pollution by DDT and γ-BHC residues of the river in this territory with a watershed area of 800 km^2.

The discrepancy between the estimated and measured concentrations of the pesticides mentioned was 40-48%.

Prediction of river water pollution by pesticide residues during spring flood was performed for the river with a watershed area of 3240 km^2.

DDT and γ-BHC concentrations in the river water were estimated twice: taking and not taking into account the storage of these pesticides in the soil.

Respectively, two above-mentioned values of the reduced runoff coefficients of pesticides were used.

The obtained concentrations of each pesticide were almost the same (to an accuracy of 10%).

The estimated average flood-period concentrations of pesticides were compared with the concentrations measured over four samples.

The predicted concentrations were twice as high as the measured ones, which appears to be associated with the fact that the water samples where the content of pesticides was measured, were collected at the end of the spring flood.

However, in detailed studies of the river water pollution by pesticides during the spring season (daily sampling), an increase in their content over the period of large water discharges was observed (3).

From these data the following relation for DDT was obtained:

$$\frac{C(t)}{\bar{C}} = \rho \frac{Q(t)}{\bar{Q}}, \qquad [7]$$

where $C(t)$ is the concentration of DDT in the river water at time *t*;

$\bar{C}$ is the average concentration of DDT in the river water during the flood period;

$Q(t)$ is the water discharge in the river at time t;

$\bar{Q}$ is the average water discharge during the flood;

ρ is the proportionality factor.

From the above it follows that the average concentration of pesticides during the spring flood was higher than the concentration obtained over four samples, according to the results of comparison.

Relation [7] can be used for predicting the daily concentrations of pesticides in river water during the spring season.

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REGULARITIES OF PESTICIDE ACCUMULATION AND MIGRATION IN THE ECOSYSTEMS OF LOWLAND RESERVOIRS

by

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Extensive use of pesticides in agriculture has resulted in their migration in terrestrial and aquatic ecosystems. At present world literature on this problem has become quite immense (I-II).

Nevertheless, there are certain gaps in the great bulk of information on the problems of pesticide turnover and migration in the biosphere. In particular, the problem of pesticide interaction with aquatic ecosystems under regulated flow conditions is still not clearly understood. Meanwhile, reservoirs are being intensively constructed in all developed countries, which inevitably affects the nature of pesticide migration in waterways.

It is well known that pesticides washed out from agricultural lands with soil runoff migrate to the very mouth of main rivers and accumulate in deltas and estuaries, especially in their biota. This regularity observed back in 50s-60s in the United States (in particular, when studying the Mississippi River) has been confirmed by our studies on the Danube, a great European river.

However, these examples refer to the rivers with practically natural flow. It is impossible to find out without special research what occurs on a river with one or more reservoirs. The difficulty of such a research lies primarily in a great variety of sources of reservoir pollution by pesticides which can enter from both global and local sources. Among these latter are agricultural lands and the industries processing agricultural vegetative raw materials; forests treated with insecticides; cities discharging domestic pesticide residues as part of sewage waters, etc.

In running water, pesticide settling to bottom sediments is insignificant. It is different in case of regulated flow where vast zones of silting begin to form and water mass movement along the river channel ceases. Under these conditions pesticide residues sorbed on suspended particles settle to the bottom, in particular in silted estuarine reaches of backwater tributaries where overgrown higher aquatic plants intensively develop. Many aquatic plants, especially reed, can extract pesticide residues from water, accumulate, metabolize and even store them up in rhizomes.

Overgrown zones act as buffers limiting the entry of pesticides from tributaries which collect their residues directly from drainage areas, into the main water area of reservoirs.

Regularities of DDT accumulation and migration have received the most study. Average concentration of DDT residues found in the organs and tissues of submersed macrophytes is typically about IO^{-2} mg/kg, whereas in rhizomes of reed and mace reed it may be as great as IO^{1} - IO^{2} mg/kg (I).

Under conditions of extensive application of pesticides in agriculture even strong buffer zones such as overgrown reed and mace reed do not protect reservoirs against pesticide contamination. This showed up most vividly as a result of an extensive use of DDT in 50s - 60s. Remote aftereffects were observed in early 70s as a noticeable increase in the content of DDT residues in all links of the trophic chains of the studied reservoir ecosystems, especially in higher links(predatory fish-zander, pike, perch).

Studies revealed that in these cases DDT residues are distributed among the elements of biota in the same way as in the other ecosystems, i.e. according to the principle of biological magnification. Increase in concentrations by this principle can be traced in food chains: zooplankton-plankton-eating predatory fish, silt - higher aquatic plants, silt - zoobenthos - benthophage fish (Table I) (2,3).

In some biotic components of the lowland reservoirs DDT residues metabolize to various levels depending on the species specificity and pollution duration. Metabolites o,p'- and p,p'-DDT (DDE and DDD) are in different proportions. In the last few years,however, there has been a shift towards prevailing metabolite DDE that is indicative of the extensive processes of metabolic transformations and a long time passed since the entry of pesticides into the reservoirs studied.

Experimental and field studies made it possible to establish some regularities of DDT accumulation and formation of its metabolites in hydrobionts at various trophic levels. In model experiments it was found that the transfer of DDT residues from water to tissues of invertebrates (Daphnia and Oligochaetae) occurred during a very short period of time - mostly in the first 24 hours. At a DDT concentration in water of I-200 μg/l Daphnia accumulated 0.25 to I8.02 mg/kg of the compound. Bottom-dwelling invertebrates (Oligochaetae) accumulated during the first day 4.3 mg/kg, 3 days - II.7 mg/kg and 6 days - 27.2 mg/kg. The lowest rate of accumulation of DDT and its metabolites was observed in mollusks of Dreissena polymorpha which contained to 2.I8 mg/kg in their tissues. In the organisms of Daphnia,

Table I. DDT content in the main components of the aquatic ecosystems studied

Groups of hydrobionts	DDT concentration, mg/kg
Higher aquatic plants (stems and leaves of Phragmites communis, Tipha latifolia, Potamogeton perfoliatus, etc.)	0.02 - 0.08
Zooplankton	0.0I - 0.04
Fish fry	0.0I - 0.02
Plankton-eating fish (roach, sardelle)	0.2 - 0.02
Fish-benthophages (bream, sazan)	0.4 - 0.6 to I.8
Predators(zander,pike)	I.5 - 6.0 to 30
Reed rhizomes	$\sim I0^{-2}$

Oligochaetae and Dreissena, mostly metabolite DDD was formed.

Systematic study of the level of DDT residue content in widespread fish species dwelling in reservoirs (zander, pike, bream, sazan, perch, carp, etc.) revealed a regular distribution of accumulated DDT and its metabolites in the organs and tissues (4). These compounds were found to accumulate mainly in fatty and brain tissues. In the internal organs(liver,stomach, intestines), prevalent were metabolites DDD and DDE, whereas DDT accumulated to a lesser extent. Minimum amounts of pesticide residues were found in muscular tissue. Experiments on feeding fish with hydrobionts poisoned by DDT showed that DDT metabolites were distributed in the organs and tissues in a similar way(Tables 2 and 3). On prolong feeding with DDT-containing nutriment, the amount of DDT increased in the lipoid - containing tissues, metabolites DDE and DDD being prevalent(5). At the same time, clinical signs of cumulative toxicosis developed, such as loss of equilibrium and motor coordination, weakening or complete loss of defensive reflexes, uncoordinated performance of fins, convulsions; fish swimmed on its side or belly up and was not mobile; in the state of agony its body was arched and gills wide-open, etc.(6,7,8). Toxicosis can proceed in two ways:

a) slow extinction of one or another predatory population (dead fish come to the surface;

Table 2. DDT accumulation in carp yearlings during its transfer through the food chain

Duration of experiment, days	Average content, mg/kg			
	DDE	DDD	DDT	Total DDT
Control		not detected		
2	0.035	0.059	0.024	0.118
5	0.111	0.081	0.081	0.274
10	0.460	0.330	0.117	0.907
15	0.885	0.647	0.212	1.744
22	1.302	1.212	0.646	3.160

Table 3. DDT accumulation in organs and tissues of perch in the model experiment

Duration of experiment, days	Organs, tissues	Average content, mg/kg			
		DDE	DDD	DDT	Total DDT
Control	Liver	0.185	0.053	0.052	0.280
	Stomach + Intestines	0.170	0.090	0.090	0.330
	Muscles		Traces		
10-12	Liver	0.520	0.010	0.02	0.532
	Stomach + Intestines	0.483	0.461	0.345	1.289
	Brain	0.330	0.456	0.205	0.991
13-20	Liver	0.360	0.270	0.038	0.668
	Stomach + Intestines	5.570	1.310	1.790	8.670
	Brain	1.122	1.015	0.563	2.700
	Muscles	0.080	0.030	0.040	0.150

b) sudden mass fish mortality (in stress situations such as water overheating, spawning, etc.).

On feeding fish with poisoned natural nutriment, toxicosis develops due to a material cumulation of DDT and its metabolites. This pesticide cumulates most intensively in the brain tissues of fish reaching critical values(4). Fish mortality occurs at a total DDT content in the brain tissue of about 3 mg/kg and over, which is in agreement with the results of the studies on similar phenomena in warm-blooded animals and birds(8,9). In this case, the most typical change is cerebral hemorrhage (9).

In experimental modeling, the clinical and pathological-anatomical picture of cumulative toxicosis can be reproduced fairly rapidly and unambiguously, the behavior of fish and clinical picture of toxicosis being similar to those of acute poisoning.

The conducted model experiments enabled us to establish the principles of DDT residue distribution in the organs and tissues of hydrobionts at various trophic levels, study cumulative toxicosis in fish, and determine characteristic features of accumulation of DDT and its metabolites depending on the functional significance of tissues and species specificity of hydrobionts.

Biochemical studies showed that the intensity of pesticide accumulation depends on the level of substance exchange typical of one or another species. Predatory fish with a higher level of metabolism have maximum accumulation. DDT metabolites are formed most intensively in the organs and tissues with a high content of lipids(liver, internal fat, brain, stomach, intestines).

Along with the effect of pesticide cumulation on high trophic links that can be shown using physiological-biochemical methods, pesticides can affect lower links of the trophic chains as well, in particular, planktonic biocenoses which response to the presence of organochlorine pesticides by changing the dominating forms of phyto- and zooplankton. In benthos, the phenomena of mass mollusk mortality were observed.

Structural changes of biohydrocenoses indicate the changes of metabolism in hydrobionts under conditions of intoxication. Experiments designed to reveal metabolic disturbances in various hydrobionts under conditions of DDT intoxication showed that the main mechanism of disturbances under the action of this pesticide and some other toxicants is the change in the content of regulators of the metabolic processes,such as vitamin B_I and nicotinamide coenzymes.For example, the content of vitamin B_I in tissues of mollusks and chironomids increased by I24–I56% under the influence of DDT. In this case, under conditions of intoxication the anaerobic processes dominated in the tissues of Dreissena and mollusks(2), as evidenced by an increasing level of the reduced forms of nicotinamide coenzymes(6).

The studies are currently being continued on the levels of accumulation of organochlorine pesticide residues in the organs and tissues of hydrobionts of lowland reservoirs. There is a distinct tendency for a sharp decrease in the levels mentioned and an increase in the numbers of food fish populations, especially predatory ones, due to the growing fry. This tendency is indicative of the improved ecological-toxicological situation in the reservoirs resulting from the effective measures on the environmental protection.

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MATHEMATICAL MODEL OF PESTICIDE EFFECTS ON AQUATIC ECOSYSTEMS

by

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The problem of pesticide effects on the environment has received widespread attention in the last few years. There is an extensive scientific literature on water and soil pollution by pesticides. Experiments are being carried out to study pesticide effects on individual species such as bacteria, algae, mollusks, fish, mammals, etc., as well as on biocenoses as a whole. It has been found that pesticides can cause biocenological changes affecting differently various organisms.

In addition to the experimental studies, attempts have been made to simulate mathematically the processes occurring in biocenoses in the presence of pesticides. For example, the authors of (7) have developed a mathematical model of the change in biological productivity of the World Ocean from I970 to I980. They investigated the effect of DDT on phytoplankton assuming that DDT substantially inhibits the mineral metabolism of microphytic algae, in particular that of nitrogen and phosphorus. It was evident from the model that as a result of the direct DDT effect alone at a concentration of I.5 μ g/l, the reproduction of feed resources and,therefore,fish take would decrease thirtyfold for ten years. Such a conclusion was drawn because of the fact that the model took no account of detoxication and possible increase in the number of competitor due to degradation of a particular species if the former was more resistant to toxins.

It has been shown experimentally (3) that pesticides increase mortality and affect motor abilities, food consumption rate and other physiological functions of the organism. According to the data presented in (5,6), the dependence of mortality on pesticide concentration can be approximated by a linear function in the area of low concentrations. At these concentrations of pesticides their effect on motor activity, food consumption rate and other functions in most cases is still insignificant and can be neglected.

In this paper we consider the model illustrating the dynamic processes in a biogeocenosis to determine qualitative changes which can occur in the living component of biogeocenoses on exposure to pesticides.

Research procedure is similar to that used previously to study water body eutrophication(2). We consider a model biocenosis consisting of two species of producers and two species of consumers, assuming that the system is closed with respect to the limiting biogenic element. M_1 and M_1' are biomasses of producers, and M_2 and M_2' are the biomasses of consumers. We assume that the biomasses of all species are expressed in units of (normalized to) the biomass of the limiting biogenic element, for example,nitrogen,phosphorus,etc. M_0 is the concentration of the limiting biogenic element in the water body. Thus, the closed system condition with respect to the substance will take the following form:

$$M_1 + M_1' + M_2 + M_2' + M_0 = M = \text{const} \qquad [I]$$

The set of equations describing the dynamics of the model biogeocenosis has the form

$$\frac{dM_1}{dt} = -\varepsilon_1 M_1 + \beta M_1 M_0 - \gamma_{12} M_1 M_2 - \delta M_1 M_2',$$

$$\frac{dM_1'}{dt} = -\varepsilon_1' M_1' + \beta' M_1' M_0 - \gamma_{12}' M_1' M_2' - \delta' M_1' M_2,$$

$$\frac{dM_2}{dt} = -\varepsilon_2 M_2 + \gamma_{21} M_1 M_2 + \delta_1 M_2 M_1',$$

$$\frac{dM_2'}{dt} = -\varepsilon_2' M_2' + \gamma_{21}' M_1' M_2' + \delta_1' M_2' M_1. \qquad [2]$$

Here ε_i are the coefficients of the mortality; β are the photosynthetic coefficients; γ_{12} and δ are the coefficients of producer uptake by consumers; γ_{21} and δ_1 are the coefficients of consumer growth.

Clearly, the qualitative behavior of the ecosystem is determined largely by the value M . When M is small,that is

$$M < \min(\varepsilon_1/\beta, \ \varepsilon_1'/\beta_1),$$

a trivial solution $M_1 = M_1' = M_2 = M_2' = 0$ turns out to be the stable solution to the set of equations [I] and [2] .

As M increases, with

$$\varepsilon_1'/\beta' > \varepsilon_1/\beta \quad \text{and } M < \varepsilon_1/\beta + \min(\varepsilon_2/\gamma_{21}, \ \varepsilon_2'/\delta_1'),$$

the stable stationary state with nonzero biomass M_1 has the form $\bar{M}_1 = M - \varepsilon_1/\beta$. As M continues to increase,the systems with two,three(and so on) species turn out to be stable. A detailed study of the analogous four-species system is given in (2,4) . Thus, we can simulate qualitatively the process of succession with weak eutrophication of the system.

Suppose there is a water body which is not inhabited at the initial moment of time and contains zero amount of biogens. Assume also that there occurs its slow enrichment with nutrients, and that small number of species M_1 , M_1' , M_2 and M_2' can migrate to this water body. Then various stable ecosystems will occur in it.

We will assign numbers to the species so that

$$\varepsilon_1'/\beta' > \varepsilon_1/\beta , \quad \varepsilon_2'/\delta_1' > \varepsilon_2/\gamma_{21} .$$

From the former inequality it follows, in accordance with the Volterra-Gauze theorem, that in the absence of other species, M_1 wins M_1' by competition. From the latter inequality it can be inferred, based on the same theorem, that in the absence of other relations, species M_2 wins by competition species M_2' when they feed on the same resources M_1 . The Volterra-Gauze theorem can be applied to the particular case given by the following set of equations:

$$\begin{aligned} dM_1/dt &= \beta M_1 M_0 - \gamma_{12} M_1 M_2 , \\ dM_1'/dt &= \beta' M_1' M_0 - \delta' M_1' M_2 . \end{aligned} \qquad [3]$$

After integrating, we can easily obtain from [3]

$$\left(M_1^{\frac{1}{\gamma_{12}}} / M_1'^{\frac{1}{\delta'}} \right) = C \cdot \exp \left[\left(\beta/\gamma_{12} - \beta'/\delta' \right) \int_{t_0}^{t} M_0 dt' \right] .$$

From this it follows, inasmuch as M_1 and M_1' are limited, that at $\beta/\gamma_{12} > \beta'/\delta'$ species M_1' is forced out.

In the general case, depending on relations between the coefficients of the set [2] , various succession series can be realized (their total number for the biocenosis studied is I6). Each of the series shows the change of stable states characterized by a certain number of species, as particular critical values of M are reached. We shall use a schematic representation of the series suggested by M.S.Polyakova (4). The limiting biogenic element M_0 always present in the system is designated by a rectangle placed at the bottom of the diagram which describes the stationary state of the system. If producers are present in the biocenosis we designate them by squares and place in the diagram directly above M_0 , and if consumers are present we designate them by squares and place above producers.

Links between the elements of the biocenosis are designated by straight lines. Relations between the coefficients also can be represented schematically by replacing with arrows the lines which indicate the links between the elements. Upward arrows designate "uptake" and downward arrows designate "pressure". For example, corresponding coefficients for "uptake" of biogenic element M_0 by producers M_1 and M_1' are ε_1/β and ε_1'/β', respectively; for "uptake" of producer M_1 by consumers M_2 and M_2' - $\varepsilon_2/\gamma_{21}$ and ε_2'/δ'; for "pressure" exerted on M_1 by consumers M_2 and M_2' - β/γ_{12} and β/δ ; and so on. Thickness of the arrows show the relations between the coefficients indicating which of the species has better "uptake" or exerts greater "pressure" on a particular species. An example of schematic representation of succession series is given in Fig.I. As seen from the figure,

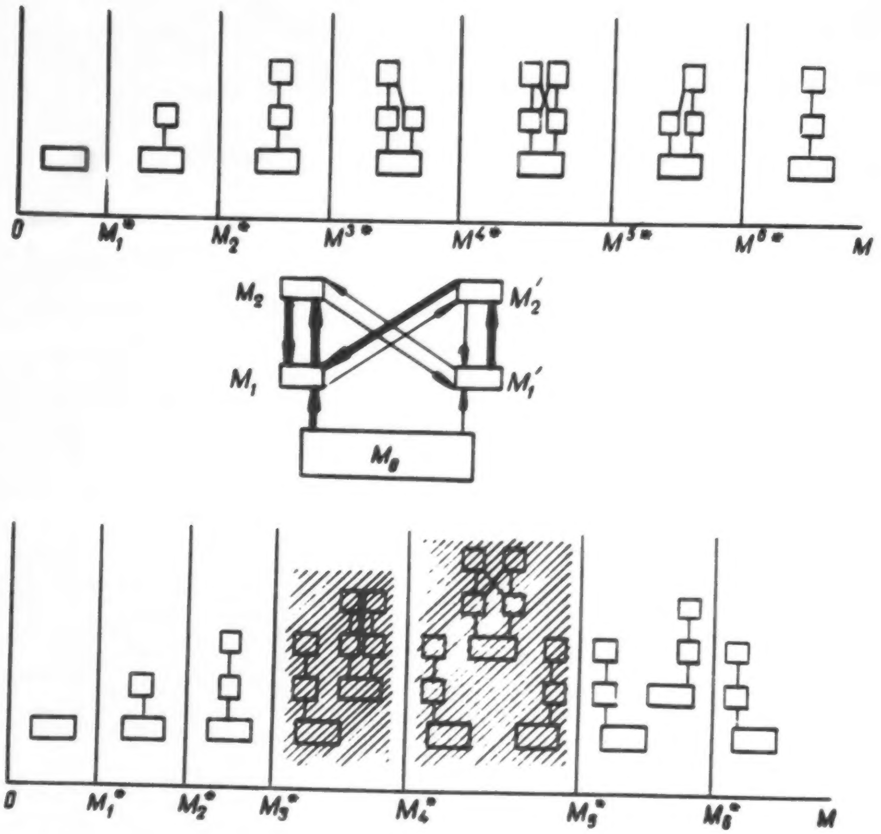

Fig.I. Examples of succession series for $(\beta + \gamma_{12})\cdot(\beta' + \gamma_{12}') > (\beta + \delta)(\beta' + \delta')$. The top series corresponds to $\delta_1 < \gamma_{21}$, $\delta_1' > \gamma_{21}'$. The bottom series corresponds to $\delta_1' > \gamma_{21}$, $\delta_1 < \gamma_{21}$.

two possibilities correspond to one and the same diagram of coefficients in accordance with two additional conditions for coefficients δ_1 , δ'_1 , γ_{21} and γ'_{21} . The first possibility is characterized by the fact that as M increases, the number of species initially increases and then decreases. Characteristic of the second possibility is the existence of triggers(dashed areas) when realization of the state depends on the initial conditions. We shall not dwell on studying the initial stage of oligotrophic-eutrophic succession, since it is discussed in some detail in (4) .

We now turn to the description of the model of pesticide effects on the change in the qualitative structure of ecosystems. As previously noted, mortality coefficients are assumed to be linearly dependent on pesticide concentration P :

$$\varepsilon_i = \varepsilon_{i0} + d_i P ,$$

where ε_{0i} and α_i are the constants characterizing properties of the i-th species. There are three types of inequalities which can vary with increasing pesticide concentration:

$$\varepsilon'_1/\beta' \gtrless \varepsilon_1/\beta ; \quad \varepsilon'_2/\delta'_1 \gtrless \varepsilon_2/\gamma_{21} ; \quad \varepsilon'_2/\gamma'_{21} \gtrless \varepsilon_2/\delta_1 \qquad [4]$$

since the quantities ε assumed to be dependent on P enter into these inequalities only.

With a small number of species(less than three), the critical values of M linearly depend on ε and,therefore, on P (I).Consequently, we have a fan of divergent straight lines in the plane (M , P) that demarcate stable states. In this case, if the character of inequalities [4] does not vary, "degradation" of the system goes through the same states with increasing P , as it went through with increasing M . This process is shown in Fig.2.

With increasing P ,however, inequalities [4] can vary, and then "degradation" follows a different path. One example is given in Fig.3. Here very interesting situations are possible. In the example considered, the stationary state with the maximum number of species occurs twice. Of interest are the examples presented in Fig.4, where, with increasing pesticide concentration, a sharp increase in the number of species occurs or no change in species diversity is observed for a long time.

Thus, a very complex change of biocenosis can be observed, as pesticide concentration increases. When added to the system, small doses of pesticides can cause not only a decrease, but also an increase in the number of species.

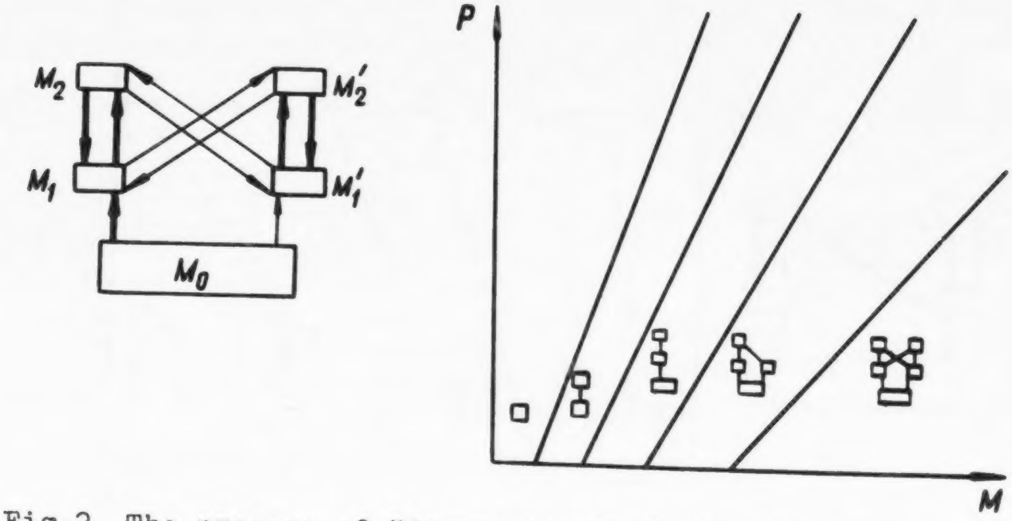

Fig.2. The process of "degradation" of the ecosystem, as the pesticide concentration increases, for $\delta_1' < \gamma_{21}$ and invariable inequalities [4]

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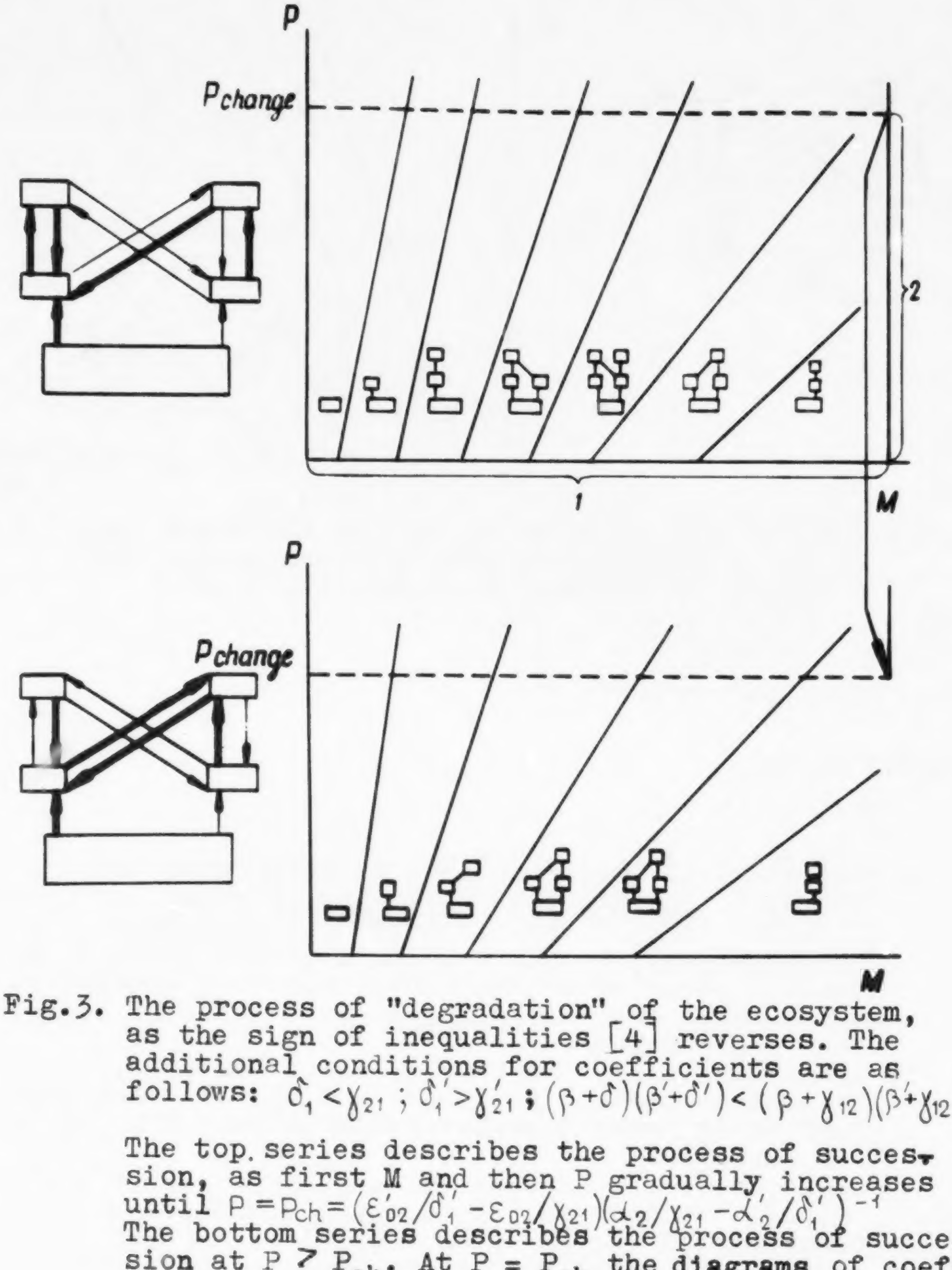

Fig.3. The process of "degradation" of the ecosystem, as the sign of inequalities [4] reverses. The additional conditions for coefficients are as follows: $\delta_1 < \gamma_{21}$; $\delta_1' > \gamma_{21}'$; $(\beta + \delta)(\beta' + \delta') < (\beta + \gamma_{12})(\beta' + \gamma_{12})$.

The top series describes the process of succession, as first M and then P gradually increases until $P = P_{ch} = (\varepsilon_{02}'/\delta_1' - \varepsilon_{02}/\gamma_{21})(\alpha_2/\gamma_{21} - \alpha_2'/\delta_1')^{-1}$ The bottom series describes the process of succession at $P > P_{ch}$. At $P = P_{ch}$ the **diagrams** of coefficients, i.e. inequalities [4], change.

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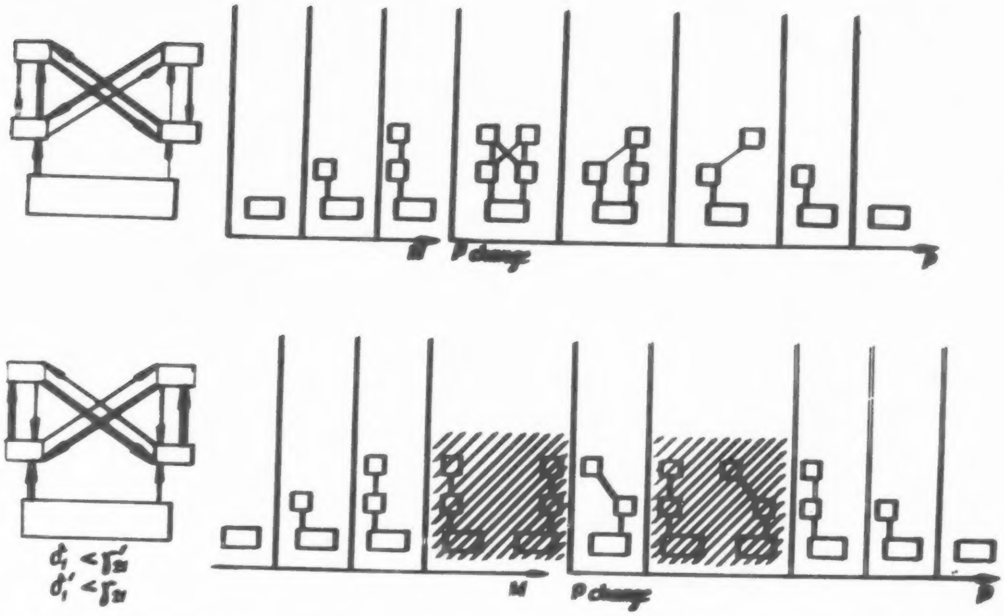

Fig.4. Examples of succession series, as the ecosystem is poisoned by pesticides. The diagrams of coefficients correspond to $P < P_{ch}$. Unlike Fig.3, the ecosystem travels in the same line, as M and P change.

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